CHLORINATION OF BIPHENYLENE WITH MOLECULAR CHLORINE AND SULPHURYL CHLORIDE

by

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It is my great pleasure to thank the University of Tripoli for a postgraduate scholarship to enable this research to be undertaken.

CONTENTS

ABSTRACT

The non-catalysed reaction of chlorine with biphenylene yields 2-chlorobiphenylene as the main product, and tetrachloro-, and trichlorohydroxy-tetrahydrobiphenylenes. Dechlorination of the tetrachloride and hydroxychloride gives biphenylene.

The reaction of biphenylene with sulphuryl chloride also gives 2-chlorobiphenylene and tetrachlorotetrahydrobiphenylene in very poor yield.

An attempt to chlorinate biphenylene with phosphorus pentachloride was unsuccessful.

2-Methoxybiphenylene has been made by combined hydrolysis and methylation of 2-benzoyloxybiphenylene. Mono- substitution occurs at the 3-position on chlorination of 2-methoxybiphenylene with molecular chlorine, giving 2-methoxy-3-chlorobiphenylene, but no chlorination occurs with sulphuryl chloride, either on standing or on reflux.

Direct chlorination of 2-nitrobiphenylene gives 2-nitro-6-chlorobiphenylene in poor yield, but nitration of 2-chlorobiphenylene gave a complex mixture.

Attempts to chlorinate 2,6-dimethoxybiphenylene, 2-chlorobiphenylene and 2-bromobiphenylene did not give identified substitution products, but chlorination of 2-chlorobiphenylene with large excess of chlorine in acetic acid gave a tetrachlorobiphenylene.

Direct chlorination of both 2-benzoyl- and 2-acetylbiphenylenes, and chlorination after sulphonation, gave an inseparable mixture of mono- and dichloro- derivatives.

2-Benzoyl-7-chloro- and 2-acetyl-6-chlorobiphenylenes were made by Friedel-Crafts benzoylation and acetylation

respectively, of 2-chlorobiphenylene.

2-Chlorobiphenylene has been made by pyrolysis of 2- and 3-chlorobiphenylene iodonium iodide* with cuprous oxide in poor yield.

Finally, pyrolysis of 4-chlorobiphenylene iodonium iodide* and 2,4-dichlorobiphenylene iodonium iodide* with cuprous oxide gave 1-chlorobiphenylene and 1,3-dichlorobiphenylene respectively.

The comparative study of the N.M.R., U.V. and I.R. spectra of the chlorobiphenylenes and those of their bromo-analogues was extensively and successfully used to distinguish between structural isomers.

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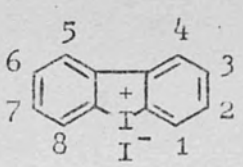
* Throughout this thesis, the following numbering system will be used.



PART ONE

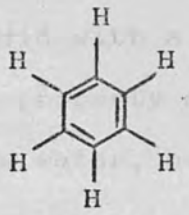
GENERAL INTRODUCTION

CHAPTER ONE*

AROMATICITY

* References for this chapter will be found on page 16.

AROMATICITY



(I)

1.1 Introduction

In the nineteenth century it was recognised that organic compounds could be classified as either aliphatic or aromatic compounds. The aliphatic compounds were designated as any compound that has an open-chain structure, while aromatic compounds were related to benzene molecules, which are cyclic.

Later, many chemists have worked hard to arrive at a satisfactory and generally acceptable definition of aromaticity[1],[2],[3] but unfortunately it is still elusive.

One definition of aromaticity is based on the reactivity of the ground-state of the molecule as a reflection of aromatic properties, and the tendency to undergo substitution reactions rather than addition reactions (benzene).

Recently, from the nuclear magnetic resonance it can be determined experimentally whether or not the compound has a closed ring of π- electrons.

1.2 Aromaticity of benzene

Benzene is said to be the great grandfather of all aromatic compounds.

Benzene was first isolated by Faraday[4] in 1825 as a pyrolysis product of a whale oil. Its chemical and physical properties are perhaps better known than those of

any other single organic compound. Benzene is a very stable, colourless liquid with a peculiar smell; it burns with a smoky flame (a property of most aromatic compounds). Benzene is insoluble in water, but is miscible with ethanol, ether, etc.

Benzene is very slowly attacked by solutions of chromic acid or acid permanganate to form carbon dioxide and water.

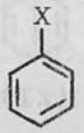
The action of chlorine on benzene depends on the presence or absence of light; in sunlight, chlorine forms addition products with benzene to form benzene hexachloride, $C_6H_6Cl_6$. In the absence of light, benzene undergoes substitution reactions to form chlorobenzene, dichlorobenzene etc.

When benzene is heated with concentrated nitric acid or concentrated sulphuric acid, it gives products of substitution.

1.3 Stucture of benzene

Analysis and molecular weight determinations show that the molecular formula of benzene is C_6H_6. The structure of benzene was proposed by Kekulé[5] in 1858, that the carbon atoms of benzene can join to one another to form a chain, but in 1865 he proposed that these carbon chains are closed to form rings. In this formulation, the six carbon atoms form hexagon structures with alternative double and single bonds (I), and all the six hydrogen atoms are equivalent. Consequently, there is only one possible mono-substituted derivative (II), but there are three disubstituted products of benzene (III - V).

Later, Ladenburg in 1869 attacked Kekule's formula on the grounds that there should be four substituted derivatives (III - VI), thus, there should be two ortho-derivatives (III) and (VI).



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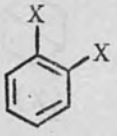

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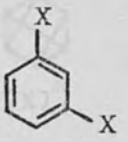

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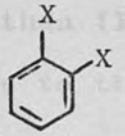

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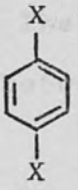
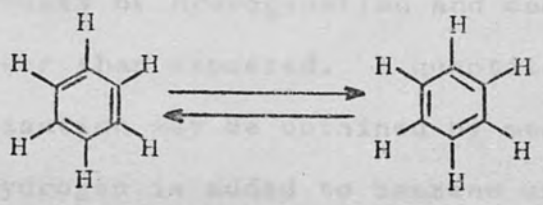


(V)

Kekulé in 1872 later pointed out that there are two equivalent hexagon structures of benzene (VII) and (VIII), which rapidly interconverted by a mechanical-motion, which is equivalent to the oscillation of the double bonds around the rings. These interchanged between (VII) and (VIII) and gave two 1,2-disubstituted derivatives, which would be in rapid equilibrium and hence could not be separated.



(VII) (VIII)

Later, in 1932, Levine and Cole[6] have supported Kekule's suggested oscillation in that they obtained on ozonolysis three different carbonyl compounds from o-xylene, which could not be obtained unless two forms of o-xylene were present.

Many other structures of benzene were proposed, such as the para bonded formulae (IX) by Dewar and Wislicenus and diagonal formulae (X) and (XI) by Claus.

(IX)

(X)

(XI)

The two Kekule's structures of benzene (VII) and (VIII) are more stable than (IX) and (XI). The instability of the latter is due to the weak bonds between the distant atoms.

The stability of benzene is found in its chemical reactions, so that benzene undergoes substitution reactions rather than addition.

Halogenation of benzene in the presence of iron gave chlorobenzene, which itself undergoes further substitution, but still has retained the characteristic aromatic properties of benzene.

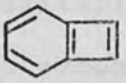
Benzene resists addition because the aromatic ring system would be destroyed.

Also the heats of hydrogenation and combustion of benzene are lower than expected. A quantitative measure of this stabilisation may be obtained by measuring the heat evolved when hydrogen is added to benzene and to cyclohexane. The same product, cyclohexane, is formed in both cases, but the heat evolved during hydrogenation in benzene is lower than in cyclohexane after allowing that benzene contains three -CH=CH- groups, while cyclohexane has just one -CH=CH- group. This means that benzene is more stable than cyclohexane.

1.4 Aromaticity in biphenylene

Biphenylene was first prepared by Lothrop[7] in 1941 by heating 2,2'-dibromobiphenyl with cuprous oxide at 350°C. Biphenylene belongs to the cyclobutadienoid series, which include cyclobutadiene (XII) and benzocyclobutadiene (XIII). Biphenylene is said to be dibenzocyclobutadiene (XIV).

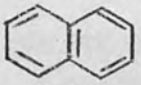
(XII)



(XIII)

The simple cyclobutadienes[8] (XII) and benzocyclobutadiene (XIII) are extremely reactive molecules, and cannot be isolated, but biphenylene (XIV) was prepared by a different route of reaction (see chapter 2).

Biphenylene is a molecule in which two benzene rings have to be joined in the ortho- positions rather than fused as in naphthalene (XV).



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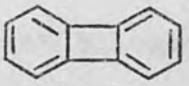


(XIV)

Biphenylene is a polynuclear aromatic hydrocarbon, which is stable in air and volatile with steam and having a faint odour. It forms complexes with picric acid[7],[9],[10], with trinitrofluorenone[11] and with nitrobenzene[12].

1.5 Structure of biphenylene

The structure of biphenylene is discussed in detail in the next chapter.

Analysis and molecular weight determination[7] show that the molecular formula of biphenylene is $C_{12}H_8$. The structure of the hydrocarbon was supported by electronic diffraction study of its vapour[13] and by X-ray crystallography

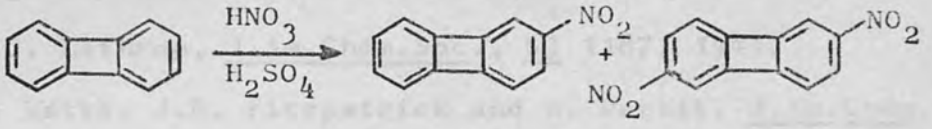
studies[14],[15],[16].

These studies confirm its planar tricyclic structure.

The arrangement of double and single bonds in biphenylene are shown (chart 2.1) and the main contributor to the resonance hybrid is the structure (d), page 29.

The reactivity of biphenylene was investigated by molecular orbital methods based on localisation energy. These show that position 2 of the hydrocarbon is more reactive towards electrophilic, nucleophilic and radical attack.

Nitration[17] of biphenylene gave mainly 2-nitrobiphenylene (XVI) as a main product with a small amount of 2,6-dinitrobiphenylene (XVII).



(XVI) (XVII)

Halogenation of biphenylene with halogens usually gives 2-halobiphenylenes but when biphenylene was treated with excess halogens it gives this time addition products rather than substitution (see later). Halogenation of a 2-substituted biphenylene, as in halogenation of 2-methoxybiphenylene to give 2-methoxy-3-halobiphenylene, arises because of biphenylene having a strongly activating substituent at position 2. This orientation was first predicted by Longuet-Higgins[18]. Chlorination of 2-nitrobiphenylene in acetic acid in light[19] gave substitution products and also addition reactions, but in the absence of light it gave only one substituted product, 2-nitro-6-chlorobiphenylene (chapter 3).

1.6 References

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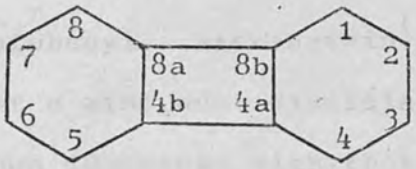
CHAPTER TWO*

BIPHENYLENE

* References for this chapter will be found on page 45.

BIPHENYLENE



2.1 Introduction

Biphenylene was first synthesised by Lothrop[1] in 1941 and it provided the first unambiguous example of a molecule containing a formal cyclobutadiene ring. It has since become a more interesting subject in regard to its chemical, physical and theoretical studies[2].

Every year since Lothrop synthesised biphenylene a new method of synthesis, and new reactions of the hydrocarbon, have been discovered.

The hydrocarbon was prepared by different methods; from biphenyl and benzene derivatives, from non-benzenoid compounds[3] and from 9-fluorenone in a discharge plasma[4].

Recently biphenylene was synthesised by pyrolysis of indazol-3-one at high temperature[5].

The arrangement of double and single bonds is shown in chart 2.1, and the best single Kekulé structure for representing biphenylene is (d), page 29.

2.2 History of biphenylene

The early history of the hydrocarbon biphenylene is a series of repeated complete failures in its preparation and of only one isolated success in 1941.

The earliest attempts to synthesise the hydrocarbon were made by Hosaeus[6] in 1893 and by Niementowski[7] in 1901.

In 1911 Dobbie, Fox and Gauge[8] claimed the preparation of biphenylene by the action of sodium in boiling ether on 2,2'-dibromobiphenyl. Nierenstein[9] at the same time also claimed that a zinc dust distillation of purpurotannin gave a hydrocarbon identical with that of Dobbie, Fox and Gauge[8].

However, attempts were continued by other workers[1],[10],[11] by replacing sodium by lithium, potassium, calcium, zinc and magnesium, and the 2,2'-dibromobiphenyl by the corresponding dichloro- and diiodobiphenyls, but these were unsuccessful.

Finally, in 1941, Lothrop[1] published his well-known paper of the synthesis of biphenylene by heating 2,2'-dibromobiphenyl with cuprous oxide at 350°C. (Biphenylene was also obtained at about the same time by Rapson and Shuttleworth) [11],[12].

2.3 Synthesis of biphenylene

a) FROM BIPHENYLS

Biphenylene was first synthesised by Lothrop[1] in 1941 by heating 2,2'-dihalobiphenyl with cuprous oxide. Poor yields were obtained when he used 2,2'-dibromobiphenyl (I), but better yields were obtained when he used 2,2'-diiodobiphenyl (II), or with biphenylene iodonium iodide[1],[13],[20] (III).

Baker and McOmie[14] studied in detail this reaction, which produced biphenylene in an approximate yield of 21% from a mixture of the two diiodides. However, higher yields (43%) could be obtained[15], which depended on the quality

of the cuprous oxide used, fresh cuprous oxide giving better yields[16],[17],[18].

Wittig and Herwig[19] found that 2,2'-diiodobiphenyl could be converted into the corresponding dilithio- derivatives (IX) which reacted with mercuric chloride to give 2,2'-biphenylenemercury (IV), and this, when heated to 300°C with silver powder, gave biphenylene in 49% yield from diiodobiphenyl.

Biphenylene was prepared recently by the conversion of 2-aminobiphenyl (V) (available commercially) into 2-iodobiphenyl (VI) by the Sandmeyer reaction.

Oxidation of 2-iodobiphenyl with peracetic acid to give 2-iodosobiphenyl (VII) is followed by cyclisation of the iodoso- compound by sulphuric acid and acetic anhydride to give biphenylene iodonium bisulphate (VIII), which is easily converted into biphenylene iodonium iodide[20] by potassium iodide. The biphenylene iodonium iodide was heated at 350°C with cuprous oxide to give biphenylene (X) (the yield based on 2-aminobiphenyl) (scheme 2.1).

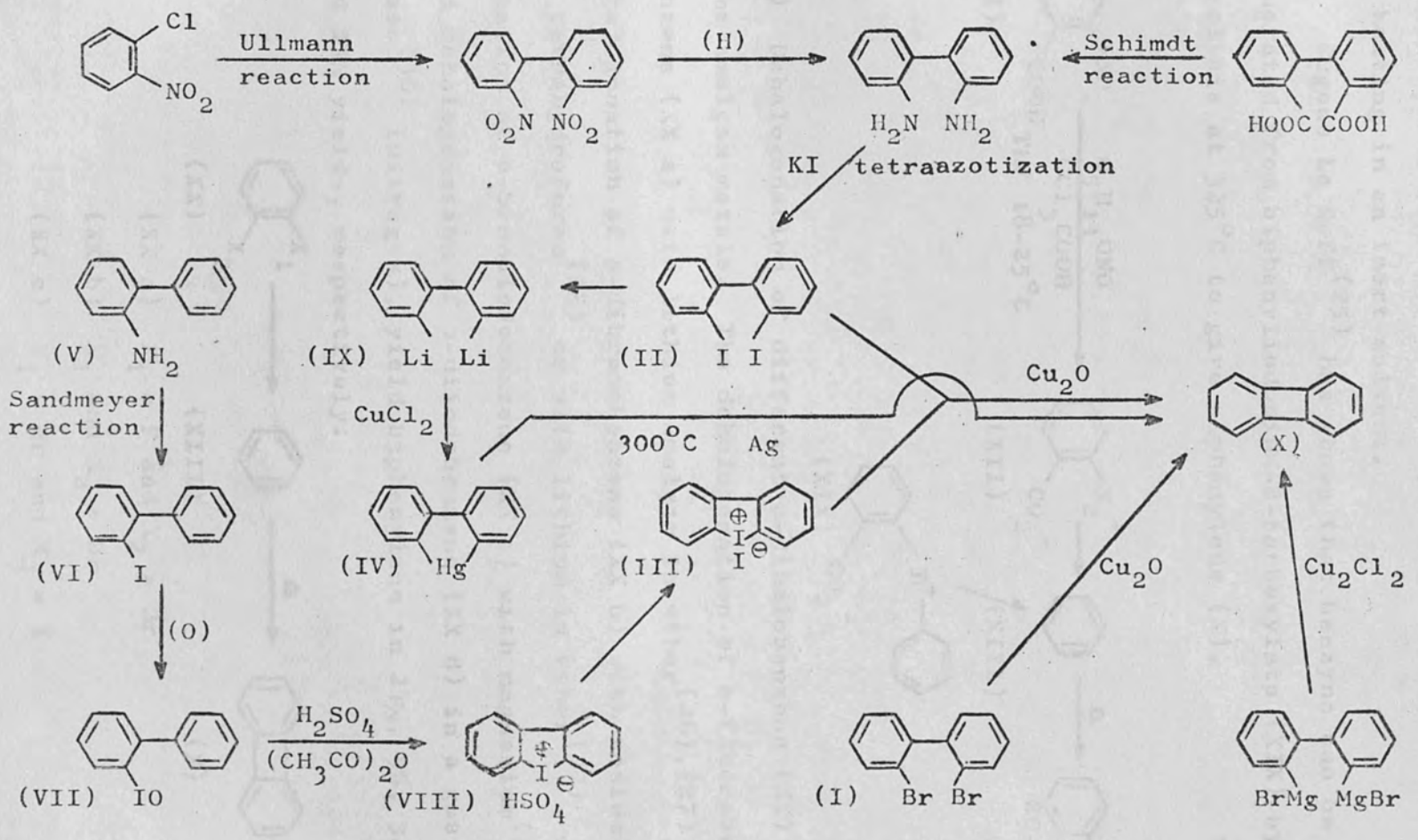
It has been assumed that cuprous oxide is the effective dehalogenating agent. However, it has recently been shown that some forms of copper powder are at least as effective as cuprous oxide[21].

Cupric oxalate has also given a high yield of biphenylene[22].

b) BY BENZYNES

Biphenylenes are produced when benzynes are generated under conditions in which they can dimerize.

There are many methods for the generation of benzynes[23]:-

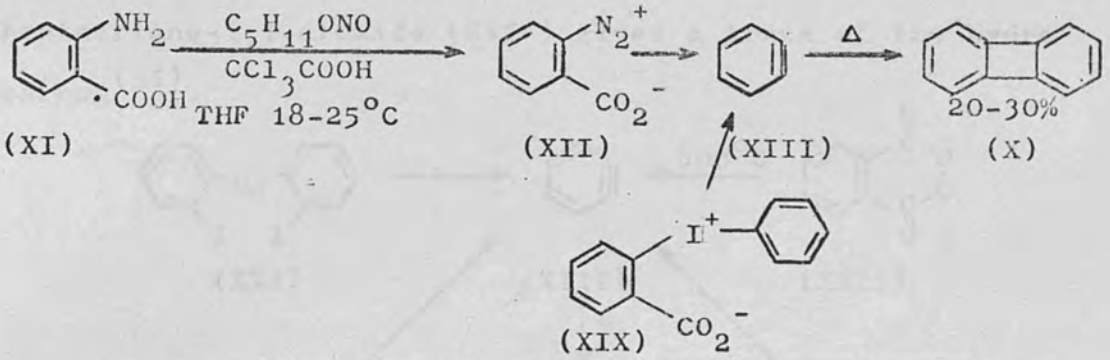


Scheme 2.1

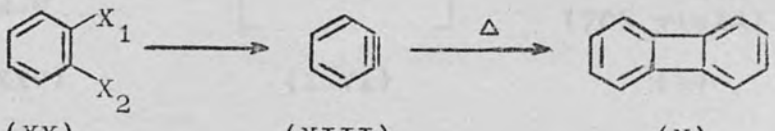
Synthetic routes of biphenylene

i) The diazotisation of anthranilic acid (XI)[24] to give benzenediazonium-2-carboxylate (XII), which can then be decomposed into benzyne (XIII), carbon dioxide and nitrogen by heating in an inert solvent.

Eugene Le Goff[25] has shown that benzyne can be generated from biphenyliodonium-2-carboxylate (XIX) by pyrolysis at 325°C to give biphenylene (X).



ii) Dehalogenation of different o-dihalobenzene (XX) with some amalgam metals. The dehalogenation of o-fluorobromobenzene (XX a) with lithium amalgam in ether[26],[27], dehalogenation of o-dibromobenzene (XX b) with sodium amalgam in tetrahydrofuran[28] or with lithium in ether[27], dehalogenation of o-bromoiodobenzene (XX c) with magnesium[29], and dehalogenation of o-diiodobenzene (XX d) in a gas phase[30] (nitrogen), yield biphenylene in 24%, 9%, 3.5% and 21% yields, respectively.



(XX) (XIII) (X)

(XX a) X_1 = F and X_2 = Br

(XX b) X_1 and X_2 = Br

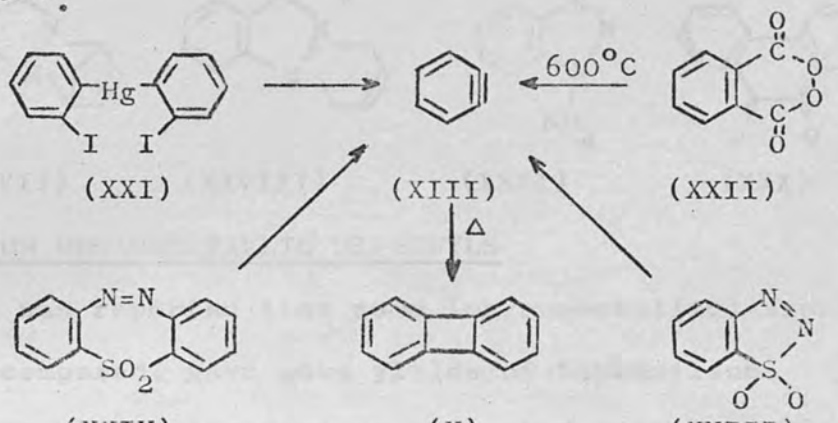
(XX c) X_1 = Br and X_2 = I

(XX d) X_1 and X_2 = I

iii) The low-pressure, gas-phase, flash pyrolysis of bis-(o-iodophenyl) mercury (XXI) and phthaloyl peroxide (XXII) at 600°C gave biphenylene in 54% and 27% yields, respectively (31).

Pyrolysis of 1,2,3-benzothiadiazole-1,1-dioxide (XXIII) in the presence of nitrous oxide gives biphenylene in 52% yield(32).

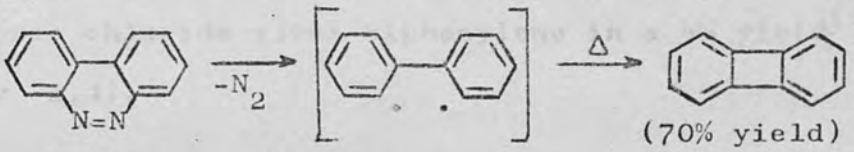
Thermolysis of 2,3,6,7-dibenzo-1-thia-4,5-diazocyclo-heptatriene-1,1-dioxide (XXIV) gives a trace of the hydro-carbon(31).



(XXI) (XIII) (XXII)

(XXIV) (X) (XXIII)

iv) MacBride(33) has prepared the hydrocarbon in high yield by vacuum pyrolysis of benzo(c)cinnoline (XXV) at high temperature. (MacBride suggested that these reactions occur by diaradical and not by fragmentation of benzyne).

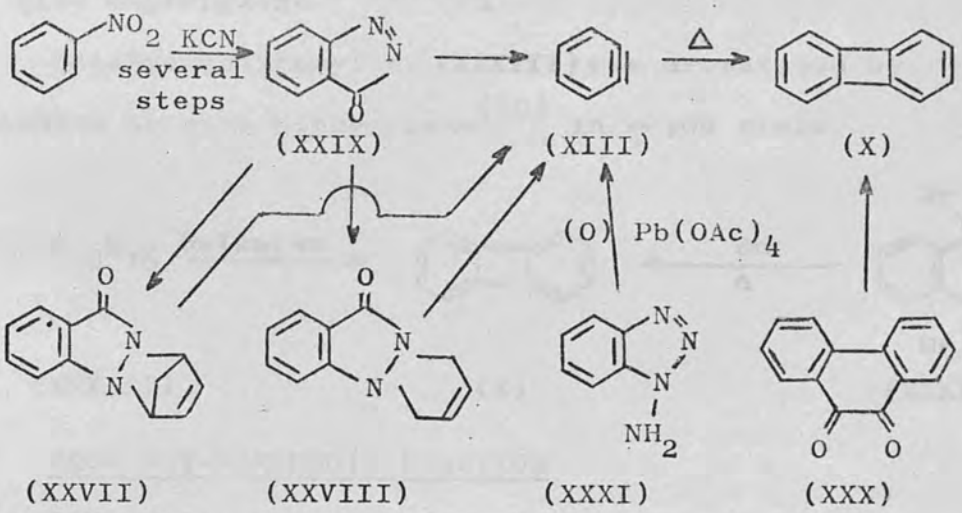


(XXV) (XXVI) (X)

Forster(5) and his co-workers also prepared biphenylene in high yield by phase pyrolysis of Diels-Alder adducts (XXVII), (XXVIII) of indazol-3-one (XXIX) at high temperature. The hydrocarbon was also obtained in poor yield (2%) by thermolysis of phenanthraquinone(34) (XXX) at 1180°C with

100μ pressure of nitrogen carrier gas.

Campbell[35] found that when 1-aminobenzotriazole (XXXI) is oxidised with lead tetraacetate, in cold benzene, biphenylene (X) is formed via benzyne in high yield (83%).



c) FROM ORGANOMETALLIC BIPHENYLS

It was reported that some (organometallic)-biphenyls, when decomposed, gave good yields of biphenylene.

When biphenylenemercury is heated with silver powder at 300°C the hydrocarbon is produced with a 54% yield[19] (Scheme 2.1) and also the photolysis[36] of biphenylene-mercury (IV) in solution gives biphenylene in 40% yield. Oxidative coupling of biphenyl-2,2'-dimagnesium dibromide with cupric chloride gives biphenylene in a 4% yield[12] (Scheme 2.1).

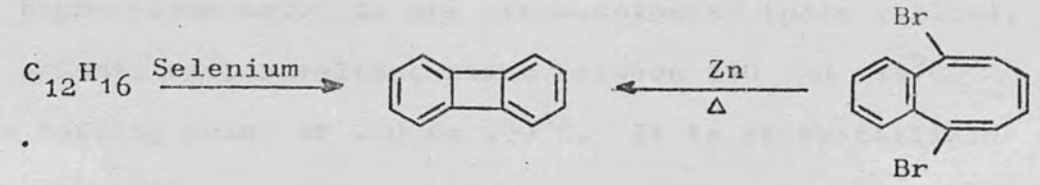
d) FROM REDUCED BIPHENYLENE

Biphenylene can be prepared from reduced biphenylene derivatives. The partial debromination of either tetra-bromobiphenylene or the hexabromide[37],[38] with sodium iodide gives 3,8-dibromobenzocyclooctatetraene (XXXII). The dibromo- compound, on heating in solvents at above 100°C,

decomposes into a mixture of biphenylene and 2-bromo-biphenylene.

Also, on heating 3,8-dibromobenzocyclooctatetraene (XXXII) with zinc dust in acetic acid, debromination occurs to give biphenylene[38],[39].

Octahydrobiphenylene (XXXIII) was aromatised by selenium to give biphenylene[40] in ~ 10% yield.

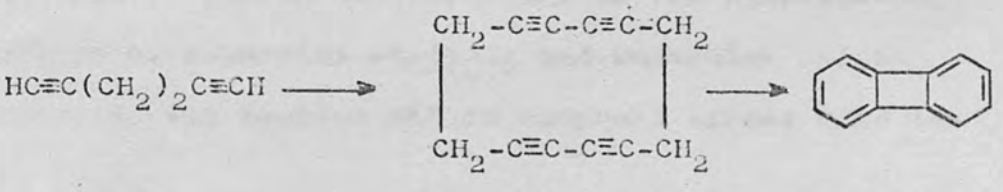


(XXXIII) (X) (XXXII)

e) FROM NON-BENZENOID REACTION

Biphenylene was produced for the first time from 'non-benzenoid' reaction[3] by oxidation coupling of 1,5-hexadiyne (XXXV) in the presence of benzene, the cyclic dimer being formed, with other compounds, which are extremely unstable.

Isomerisation of the cyclic dimer (XXXIV) in pentane-ether, with saturated solution of potassium t-butoxide in t-butyl alcohol, at room temperature, gives an impure mixture, which is purified by column chromatography to give biphenylene in 7.4% yield.



(XXXV) (XXXIV) (X)

2.4 General properties of biphenylene

1. PHYSICAL PROPERTIES

Biphenylene is a typical tricyclic aromatic hydrocarbon. It is quite stable in the air and it is not easily decomposed by heat. Biphenylene shows no more tendency to undergo addition reactions than do other polycyclic hydrocarbons.

Biphenylene crystals are straw-coloured (pale yellow), long prisms, with a melting point between 110 and 111°C, and a boiling point of 260 to 280°C. It is recrystallised from methanol.

It is volatile with steam, sublimes easily, has a faint odour, similar to biphenyl, and forms a crystalline complex with picric acid[1],[12],[28], trinitrofluorenone[14] and trinitrobenzene[31].

2. STRUCTURE

a) From chemical method

The structure of biphenylene is formally the dibenzo-derivative of cyclobutadiene. This was proved by Lothrop[1] and confirmed by Baker and McOmie[14].

Lothrop[1] proved the structure of the hydrocarbon biphenylene by elemental analysis and molecular weight determination (in benzene and in camphor) agrees with the formula $C_{12}H_8$.

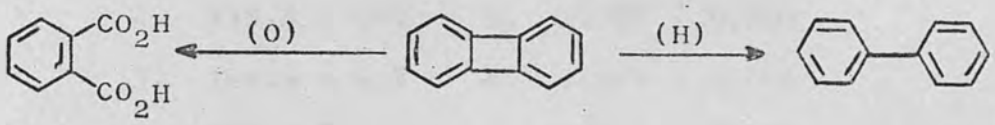
The most convincing evidence of its structure was the oxidation of the hydrocarbon with chromic oxide to give phthalic acid (XXXVI) and when its vapour was mixed with hydrogen and passed over red hot copper catalyst, biphenyl

(XXXVII) was given.

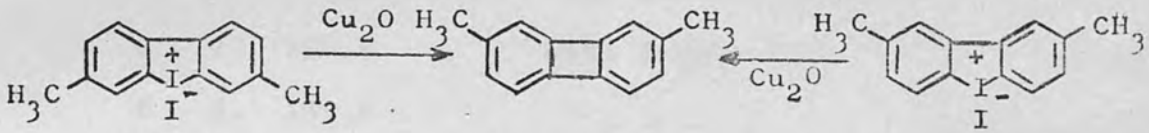
Lothrop[1] synthesised a substituted biphenylene from either of two appropriately substituted 2,2'-dihalobiphenyls.

So Lothrop[1] prepared 2,7-dimethylbiphenylene (XXXVIII) by pyrolysis of either 3,6-dimethylbiphenyleneiodonium iodide (XXXIX) or 2,7-dimethylbiphenyleneiodonium iodide (XXXX) with cuprous oxide at 350°C.

This shows that the biphenylene molecule possesses at least one plane of symmetry.



(XXXVI) (X) (XXXVII)



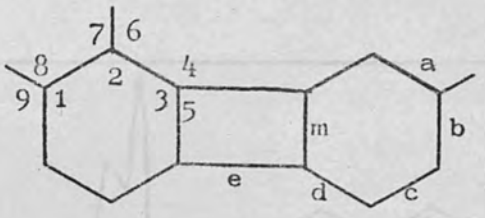
(XXXX) (XXXVIII) (XXXIX)

b) From physical methods

The structure of biphenylene was supported by electron diffraction studies of the vapour[41] and by X-ray crystallography[42],[43],[44] studies, which have given precise bond lengths and angles, as shown on page 29. More recently, X-ray studies by Yokozeki and his co-workers[45] in the gas phase are in good agreement with corresponding values derived from a crystal structure analysis. These studies confirmed that the hydrocarbon is a planar, tricyclic structure, and that the central bonds (m and e), that join the two six-membered rings, are significantly longer than the bonds (a, b and d) that make up the rings. These measurements are supported by chemical evidence[46].

The arrangement of double and single bonds in biphenylene was shown (chart 2.1), by five canonical forms.

The main contributor to the resonance hybrid is the structure (d).



Bond angles (°)		Bond length (Å)	
1.	122.2 ± 0.2	a.	1.423 ± 0.003
2.	115.2 ± 0.2	b.	1.385 ± 0.004
3.	122.6 ± 0.2	d.	1.372 ± 0.002
4.	147.4 ± 0.2	e.	1.514 ± 0.003
5.	90.0 ± 0.2	m.	1.426 ± 0.003
6 - 7.	122.0	C-H	1.060
8 - 9.	119.0		

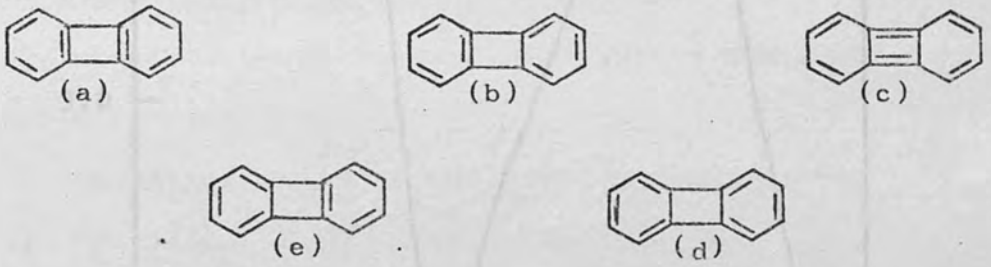


Chart 2.1
Canonical resonance forms of biphenylene

The ultra-violet spectrum[14],[47],[48] shows two main absorptions at 235-260 mu and 330-370 mu (Fig. 2.1) and is that expected of tricyclic aromatic systems (biphenyl exhibits only one absorption at 250 mu) (see Table 2.1).

The nuclear magnetic resonance spectrum studies confirm that there is little interaction between the two six-membered rings[49],[50],[51].

The infra-red spectrum[52],[53],[54] of biphenylene is

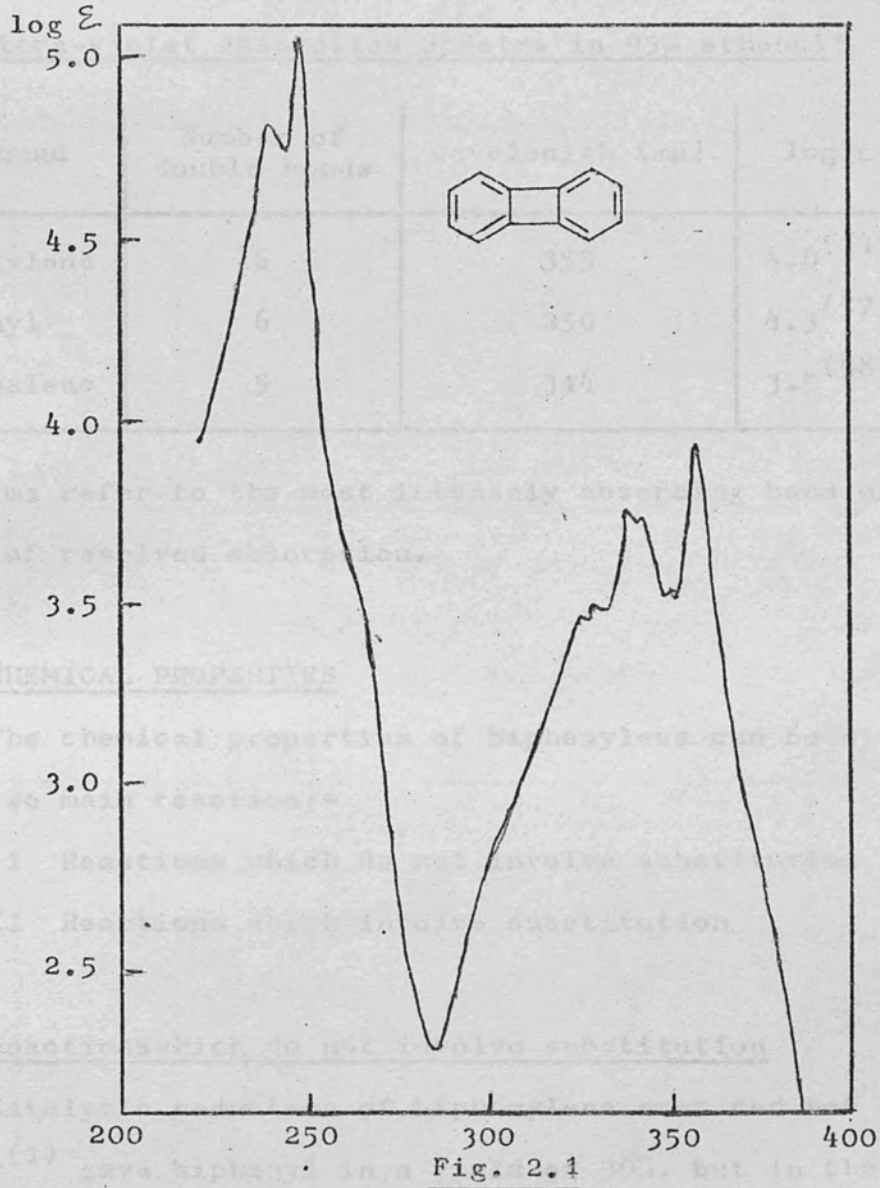


Fig. 2.1

Ultra-violet Absorption of biphenylene in ethanol

consistent with the o-disubstituted benzene formula, although the mass spectrum shows a molecular ion (m/e = 152) which is thought to be a product of ring-opening[55],[56].

Table 2.1

Ultra-violet Absorption Spectra in 95% ethanol*

Compound	Number of double bonds	Wavelength (mμ)	log ε
Biphenylene	6	355	4.0[14]
Biphenyl	6	250	4.3[57]
Naphthalene	5	314	3.5[58]

* Maxima refer to the most intensely absorbing band of each group of resolved absorption.

3. CHEMICAL PROPERTIES

The chemical properties of biphenylene can be divided into two main reaction:-

I Reactions which do not involve substitution

II Reactions which involve substitution

(I) Reactions which do not involve substitution

Catalytic reduction of biphenylene over red hot copper[1] gave biphenyl in a yield of 30%, but in the presence of Raney nickel[14] in alcoholic solution the yield is increased to 85%.

Biphenylene is also reduced with sodium and liquid ammonia to give biphenyl (see page 40). It is not reduced by amalgamated zinc[14] and hydrochloric acid (or by cyclohexadiene[26]).

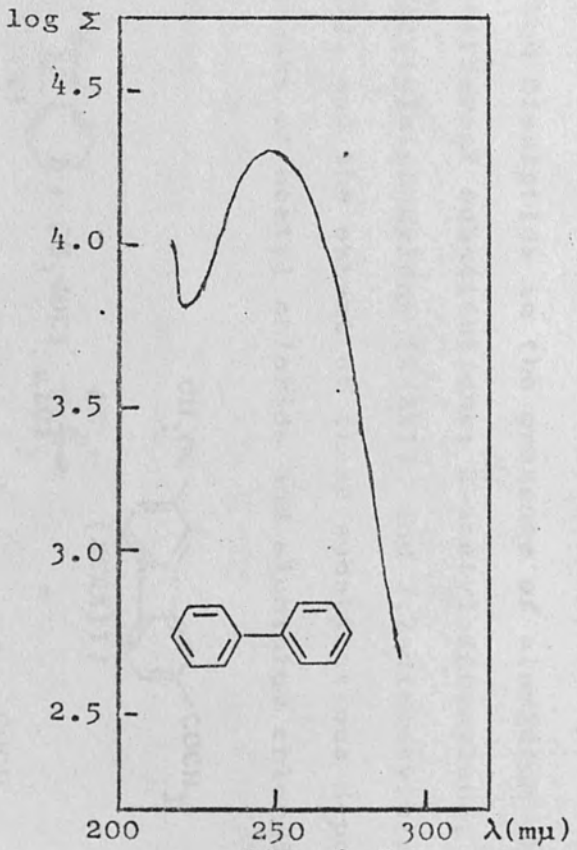


Fig. 2.2

Ultra-violet Absorption of biphenyl in ethanol

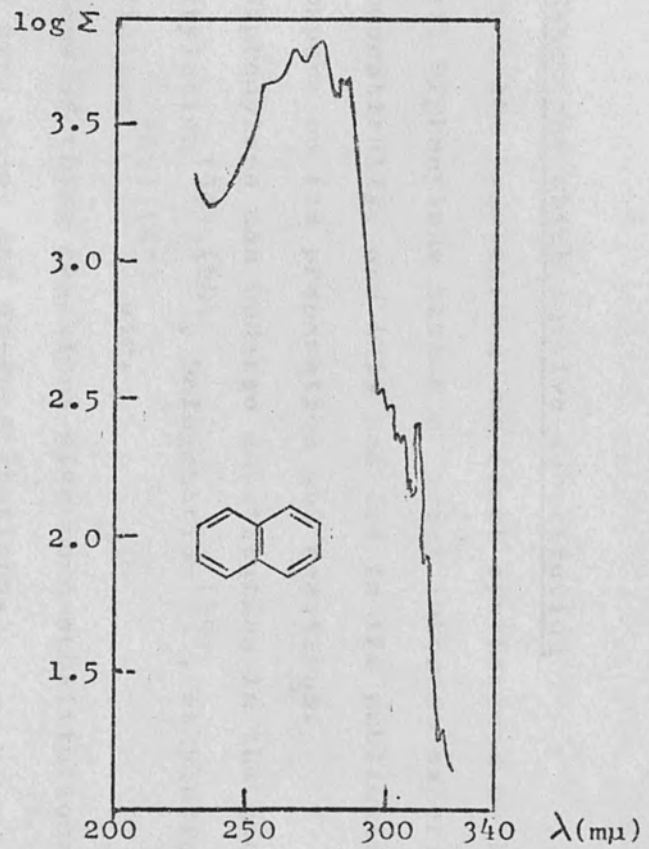


Fig. 2.3

Ultra-violet Absorption of naphthalene in 95% ethanol

Oxidation of biphenylene by chromic oxide[1] in acid solution at room temperature gives phthalic acid, and also when the hydrocarbon is refluxed with dilute nitric acid phthalic acid is obtained.

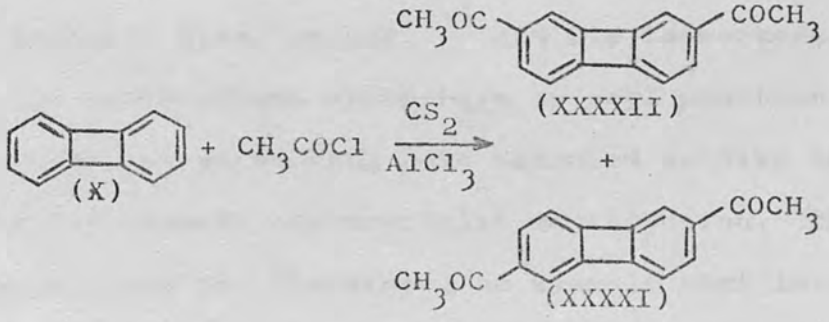
(II) Reactions which involve substitution

When the hydrocarbon was first synthesised by Lothrop[1] in 1941, biphenylene became of great interest experimentally and theoretically, and this has led to the publication of more papers on its preparation and reactions.

Biphenylene can undergo substitution in the nucleus by acetylation[59],[60], halogenation[59], ethylation[61], benzoylation[62],[63] etc.

Some of these reactions give mono-substitutions, others give mono- and di-substitutions.

Acetylation[60] of biphenylene with acetyl chloride in carbon disulphide in the presence of aluminium chloride gives different substitutions; 2-acetylbiphenylene, 2,6-diacetylbiphenylene (XXXXI), and 2,7-diacetylbiphenylene (XXXXII), and the extent of these substitutions depends on the amounts of acetyl chloride and aluminium chloride used.



Bromination[37-38] of biphenylene with bromine in acetic acid gives 2-bromobiphenylene, tetrabromo- compounds

and two hexabromo- compounds (see pages 42-43).

The reactivity of biphenylene has recently been based on localization energies, and this leads to the prediction that the 2-position should be the more reactive towards electrophiles, nucleophiles and radicals, even though the free valence is slightly higher at the 1-position (0.43) than at position 2 (0.41).

The addition of an attacking species of biphenylene, which form the Wheland intermediate, which are hybrids of ions (a, b, c) and (d, e, f) respectively (chart 2.2). Suppose that these canonical forms have cyclobutadiene characters in the four-membered ring and are the least stable, then the two forms (a) and (c) have more energy for 1-substitution and (f) has less energy for 2-substitution and is more stable.

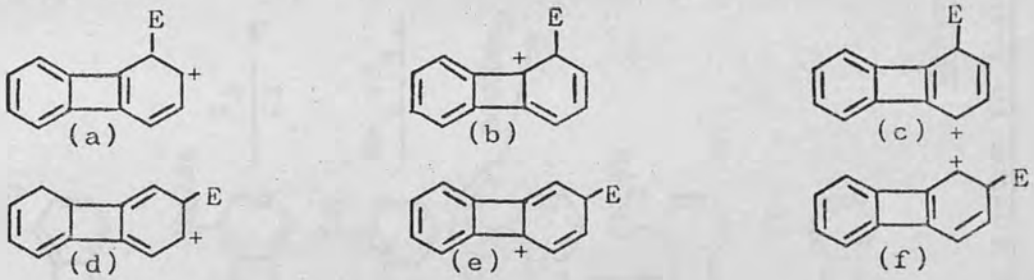
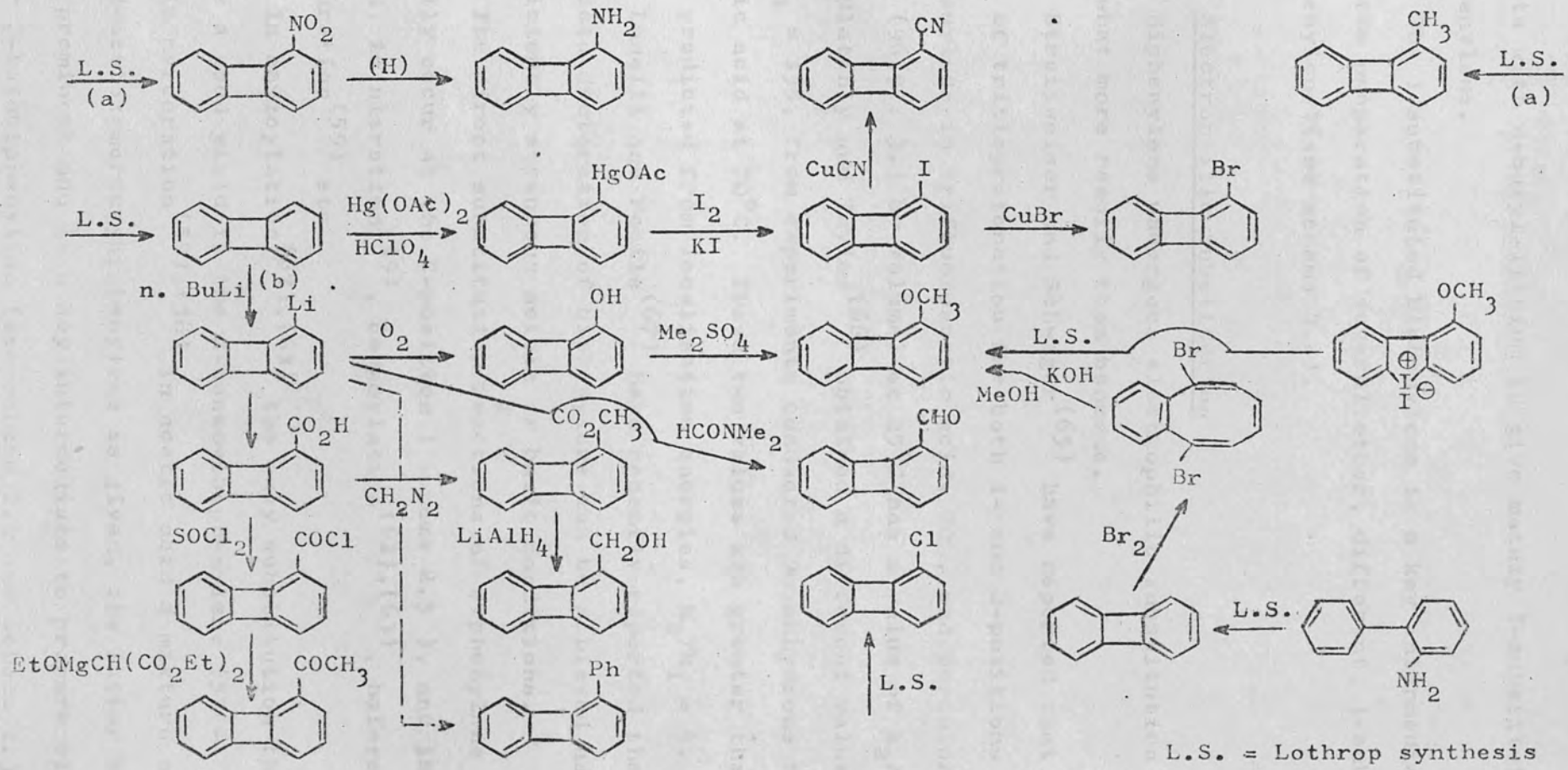


Chart 2.2

Resonance-stabilised carbonium ions of biphenylene

Recently Streitweiser[51] and his co-workers found that the hydrocarbons which have an aryl position adjacent to a fused, strained ring have enhanced acidity and reduced reactivity towards electrophilic substitution. The 1-position of biphenylene is, therefore, an example that in protodetritiation with lithium cyclohexylamide in cyclohexylamine at 50°C, it is 79 times more reactive than the 2-position.

Boulton[64] and his co-workers found that biphenylene



L.S. = Lothrop synthesis

Scheme 2.2

Synthetic routes to 1-substituted biphenylenes

reacts with n-butyl-lithium to give mainly 1-substituted biphenylene.

The 1-substituted biphenylene is a key intermediate for the preparation of several other, different, 1-substituted biphenylene (see scheme 2.2).

a) Electrophilic Substitution

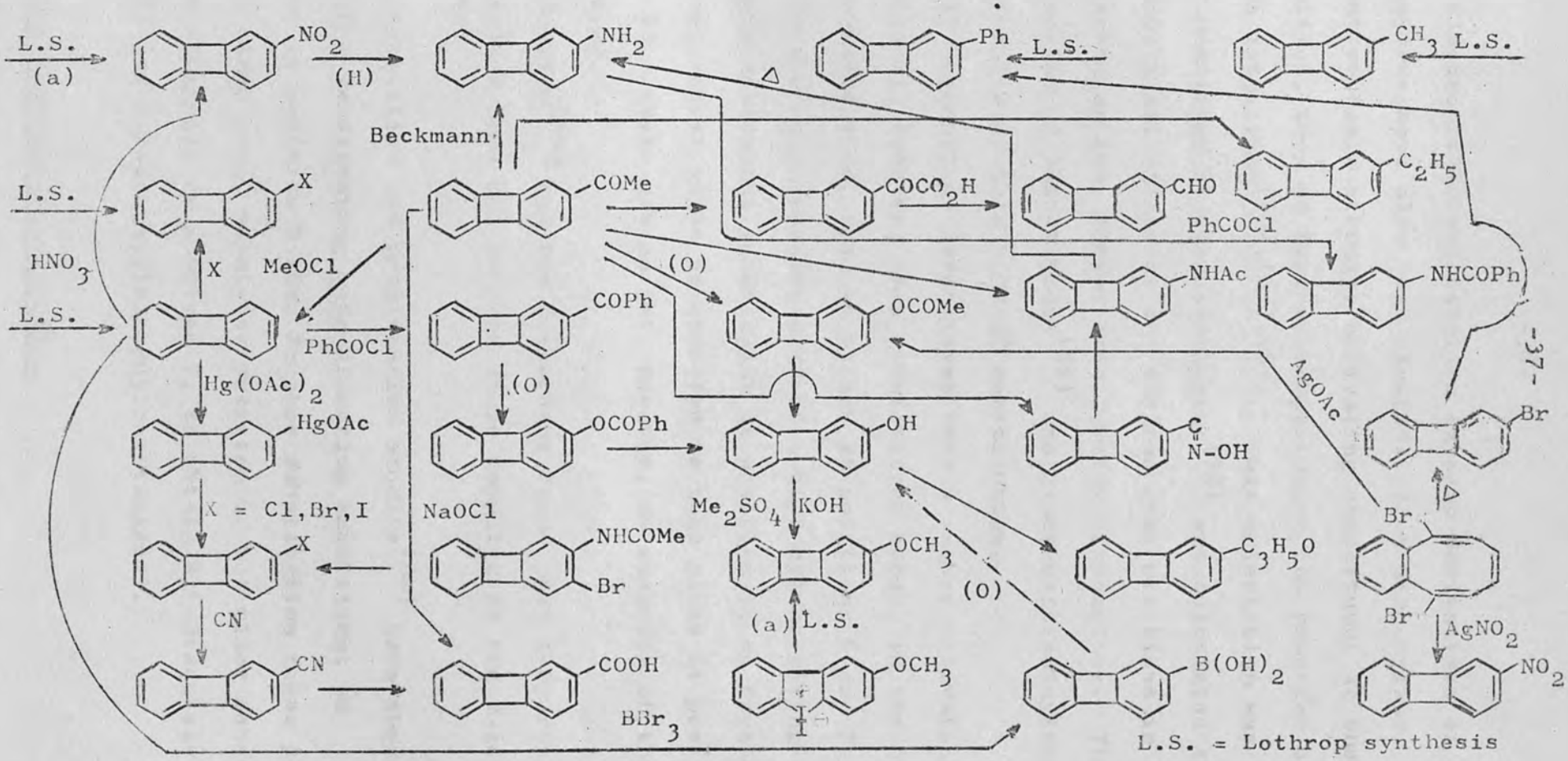
Biphenylene undergoes electrophilic substitution somewhat more readily than benzene.

Streitweiser and Schwager[65] have reported that the rate of tritioprotonation for both 1- and 2-positions of biphenylene in trifluoroacetic acid, 70%, and perchloric acid (96.9 : 3.1 by volume) at 25°C has a value of $k_2/k_1 = 64$, but Blatchly and Taylor[66] obtained a different value, $k_2/k_1 = 135$, from experiments conducted in anhydrous trifluoroacetic acid at 70°C. These two values are greater than the rate predicted from localisation energies, $k_2/k_1 = 4$.

Lunelli and Pecile[67] have recently reported that complete deuteration of biphenylene can be achieved using sufficiently strenuous acidic or basic conditions.

The direct substitution reactions of biphenylene usually occur at the 2-position (scheme 2.3), and in good yield, in nitration[59], benzoylation[62],[63], halogenation[59], mercuration[59] etc.

In benzoylation[62],[63] the only substitution that gives a good yield is the 2-benzoylbiphenylene (59 - 80%), but in mercuration[59],[38] in acetic acid a mixture of 1- and 2-acetoxymercurybiphenylene is given, the latter being more prominent and is a key intermediate to prepare either 1- or 2-halobiphenylene (see scheme 2.2 and scheme 2.3).



Scheme 2.3

Synthetic routes to 2-substituted biphenylenes

Electrophilic substitution in some derivatives of biphenylene have also been studied. If a biphenylene derivative has a strongly activating substituent at the 2-position, then on further substitution the reaction occurs at the 3-position[46],[68],[69]. This orientation was first predicted by Longuet-Higgins[70] who calculated the electron availability at the various ring positions in the carbonium ion, formed from 2-methylbiphenylene. The bromination of 2-acetamido-[46] and 2-methoxybiphenylene[69] are examples of this kind of substitution.

If biphenylene derivatives have a weaker activating substituent, however, some substitution occurs in the other six-membered ring, open to attack at positions 6 and 7.

In the corresponding case of a biphenylene having a strongly activating substituent at position 1, on further substitution it might be expected to take place at position 2 (or 4). There are as yet, however, no examples of this occurring.

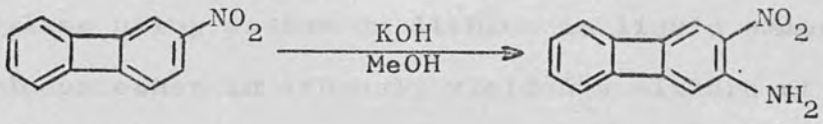
Boulton[64] and his co-workers found that 1-hydroxybiphenylene does not undergo diazo coupling as the 2-isomer does[63].

Acetylation and propionation studies[60] have shown that if a deactivating meta-directing substituent is present at position 2 then further substitution takes place in the other ring, mainly at position 6, but minor substitution occurring at position 7, to obtain 2,6-diacetyl- (XXXXI) and 2,7-diacetylbiphenylene (XXXXII).

b) Nucleophilic Substitution

No certain examples of nucleophilic substitution have

been reported for biphenylene. Barton[71] reported that nucleophilic amination of 2-nitrobiphenylene (XXXXIII), which undergoes attack at position 3, gave 2-amino-3-nitrobiphenylene (XXXXIV) but 1-nitrobiphenylene was unreactive under the same conditions. Barton proposed the mechanism on the analogy of the amination of nitronaphthalene[72]



(XXXXIII) (XXXXIV)

c) Homolytic Substitution

Homolytic aromatic substitution in biphenylene has been little studied[59]. Biphenylene reacts with lead tetraacetate in acetic acid[54],[73] with difficulty to give 2-acetoxybiphenylene in poor yield (1.5%).

Recently Dickerman[74] and his co-workers have found that the phenylation of biphenylene occurs at both positions 1 and 2 to give 1-phenylbiphenylene and 2-phenylbiphenylene.

d) Addition Reactions

1. Rupturing of the four-membered ring

a) HYDROGEN

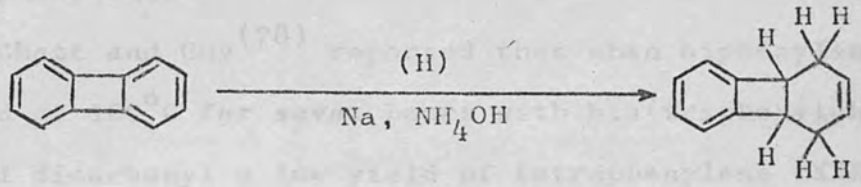
The reduction of biphenylene with hydrogen over a red hot copper catalyst[1], and with Raney nickel in alcohol as solvent[1] at room temperature, causes the four-membered ring to open giving biphenyls.

The reductive ring opening is characteristic of

biphenylene and its derivatives, and does in fact occur under very mild conditions[52].

Recently Barton[75] found that the reduction of biphenylene using metal-amine systems gives biphenyl in 85% yield and other products, according to the vigour of the reaction.

More recently Matuszak[76] found that the reduction of biphenylene using sodium or lithium in liquid ammonia, plus anhydrous ether in ethanol, yielded a mixture of unreacted biphenylene (X) and 1,4,4a,8b-tetrahydrobiphenylene (XXXXV) and other products, but biphenyl was not found.

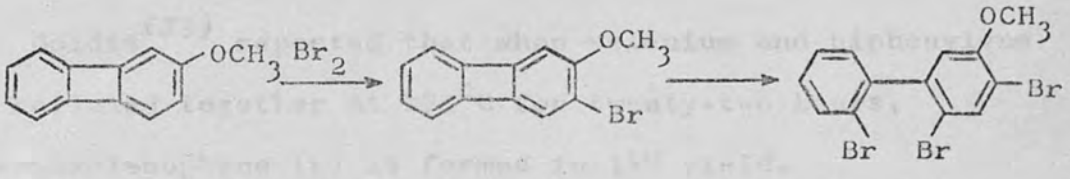


(X) (XXXXV)

b) BROMINE

The addition of bromine to certain biphenylene derivatives gives derivatives of biphenyl, but with the parent hydrocarbon and bromine a substituted biphenylene is formed (2-bromobiphenylene) instead of the addition reaction.

Bromination of 2-methoxybiphenylene[69] (XXXXVI) with excess bromine in acetic acid gives 2,2',4-tribromo-5-methoxybiphenylene (XXXXVII).

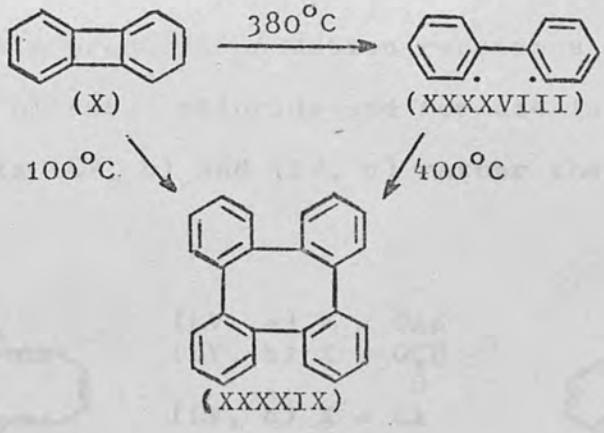


(XXXXVI) (XXXXVII)

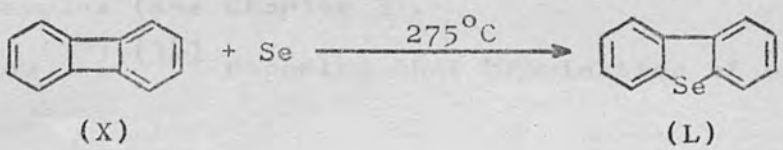
c) TEMPERATURE

Friedman[55],[56],[77] and his co-workers have studied the reaction of biphenylene at high temperatures. When biphenylene is heated at 400°C diradicals (XXXXVIII) are formed which then dimerize to tetraphenylene (XXXXIX) in 96% yield, but when heated to 340°C the yield of tetraphenylene is decreased to 8%. The effect of time and temperature on the reaction gives different products. Lower temperatures result in decreased conversion of biphenylene,, but by extending the reaction time, however, biphenylene is gradually consumed without significant formation of tetraphenylene.

Chatt and Guy[78] reported that when biphenylene is heated at 100°C for seven hours with bis(triphenylphosphino)-nickel dicarbonyl a low yield of tetraphenylene (XXXXIX) is given while with chromium hexacarbonyl at 255°C fluorenone and another product is given.



Gaidis[79] reported that when selenium and biphenylene are refluxed together at 275°C for twenty-two hours, dibenzoselenophene (L) is formed in 14% yield.

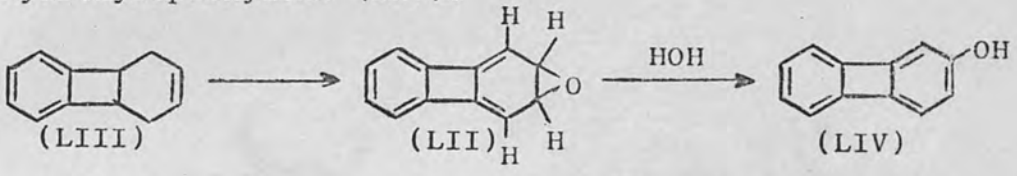


2. Addition to the six-membered rings

Addition to the six-membered rings (2-3 bond) of biphenylene has been studied by Baker[14] who recorded that the reaction of biphenylene with ethyl diazoacetate gives a low yield of a carboxylic acid after hydrolysis.

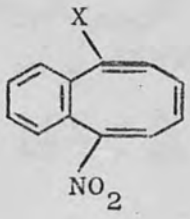
Kende and MacGregor[80] have reinvestigated the same reaction and shown the product to be the ethyl ester of fluorene-2-carboxylic acid (LI).

Gunther and his co-workers[81] have reported that they have synthesised 2,3-epoxybiphenylene (LII) for the first time, starting from 1,4,4a,8b-tetrahydrobiphenylene (LIII) in 47% yield. The epoxybiphenylene, on hydrolysis, gave 2-hydroxybiphenylene (LIV).



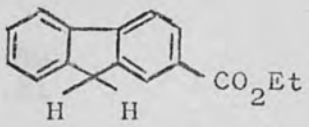
(LIII) (LII) (LIV)

The nitration of biphenylene with nitric acid in acetic anhydride gives 3-acetoxy-8-nitrobenzocyclooctatetraene[82] (LV, a) as the main product. Addition reactions of biphenylene with nitrosyl chloride and formate lead to analogous products (LV, b) and (LV, c) rather than nitroso-compounds.



(LV)

(LV, a) X = OAc
(LV, b) X = OCH (O)
(LV, c) X = Cl



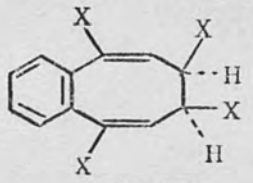
(LI)

Halogenation of biphenylene in the absence of light is very complex (see Chapter 3).

Barton[37],[38] reported that bromination of biphenylene

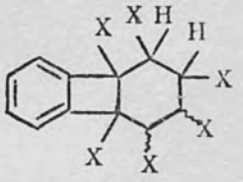
(in light) in carbon tetrachloride gave three addition products, a tetrabromide (LVI, a) and two closely similar hexabromides (LVII,a) but bromination in acetic anhydride gave two addition products, a dibromo- compound (LVIII, a) and tetrabromo-tetrahydrobiphenylene.

Whitaker[83] has studied the reaction of biphenylene with molecular chlorine (in light) which gave a similar mixture of two tetrachlorides (LVI, b) and (LIX, b) and three hexachlorides (LVII, b) and acetoxypentachloride (LX), while the reaction of biphenylene with sulphuryl chloride[85] gives a low yield of dichloro- compound (LVIII, b) together with a mixture of chlorobiphenylenes.



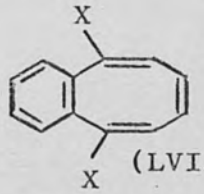
(LVI)

(LVI, a) X = trans-Br
(LVI, b) X = cis-Cl



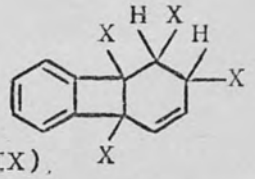
(LVII)

(LVII, a) X = Br
(LVII, b) X = Cl



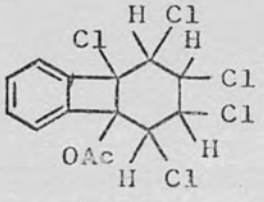
(LVIII)

(LVIII, a) X = Br
(LVIII, b) X = Cl



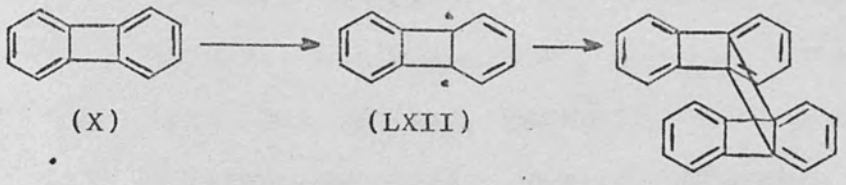
(LIX)

(LIX, a) X = Br
(LIX, b) X = Cl



(LX)

Goldman[80],[84] and his co-workers have shown that when biphenylene solution (hexane) is irradiated with a 275 watt sun-lamp for three days a photodimer (LXI) is given and he proposed that the coupling occurred at positions 4a and 8b in both molecules, probably via diradical (LXII).



(X) (LXII) (LXI)

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PART TWO

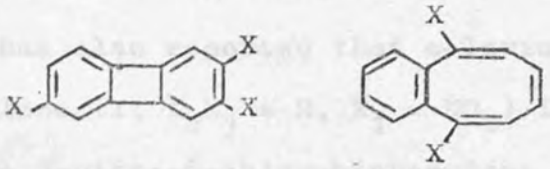
MAIN SECTION

CHAPTER THREE*

CHLORINATION OF BIPHENYLENE

* References for this chapter will be found on page 97.

CHLORINATION OF BIPHENYLENE



(I) (II)

3.1 Introduction

The chlorination of biphenylene has been studied a little by Baker et al[1], who found that chlorination of biphenylene in carbon tetrachloride in the presence of iodine gave a complex mixture, but when biphenylene was boiled with iodine monochloride in acetic acid, 2-chloro-biphenylene (IX) was obtained in good yield.

Later, Whitaker[2] repeated the molecular chlorination, but without a catalyst and when the reaction mixture was irradiated with U.V. light again a complex mixture was obtained. This mixture was separated into its addition compounds by column chromatography to give a tetrachloride (X) and two stereo-isomeric hexachlorides (XI).

A similar reaction in glacial acetic acid gave five addition components, another tetrachloride (XII), three stereo-isomeric hexachlorides (XI) and acetoxypentachloride (XIII) (scheme 3.2).

Whitaker has attempted to prepare the dichloride (II, X = Cl) by the chlorination of biphenylene in acetic acid-acetic anhydride in a freezing mixture, but was unsuccessful[2].

Barton[3] has prepared a dichloride (II, X = Cl) by the action of sulphuryl chloride on biphenylene, and from U.V. and N.M.R. spectra studies it has been shown to have

an expanding ring structure identical with that of 3,8-dibromobenzocyclooctatetraene (II, X = Br)[4].

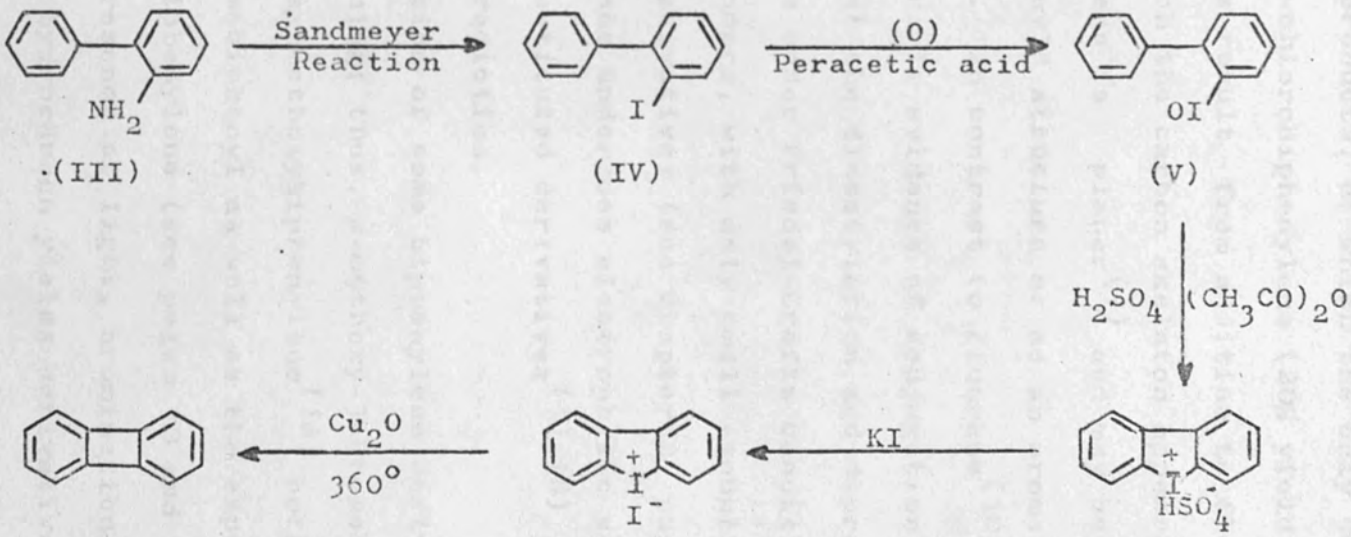
Whitaker has also reported that chlorination of 2-nitrobiphenylene (I, X_2X_3 = H, X_1 = NO_2) in acetic acid with light gave 2-nitro-6-chlorobiphenylene (I, X_1 = NO_2, X_2 = H, X_3 = Cl) and nitro-acetoxypentachloride.(LX)

There is no report on the chlorination of 2-methoxybiphenylene[5] (X_1 = OMe, X_2X_3 = H) but bromination gave 2-methoxy-3-bromobiphenylene[6] (I, X_1 = OMe, X_2 = Br, X_3 = H) as a main product.

3.2 Chlorination of biphenylene

Biphenylene (VIII) was prepared by Lothrop's method[7] starting from 2-aminobiphenyl (III) (available commercially) which was converted into 2-iodobiphenyl (IV) by the Sandmeyer method, followed by oxidation of the latter biphenyl with peracetic acid to give 2-iodosobiphenyl (V). This iodoso-compound was cyclised by sulphuric acid and acetic anhydride to give biphenylene iodonium bisulphate (VI), which was then converted into biphenylene iodonium iodide (VII) when treated with potassium iodide. Finally, pyrolysis of biphenylene iodonium iodide (VII) with cuprous oxide at 360°C gave biphenylene in 60 - 70% yield (scheme 3.1). The yield of biphenylene depended, rather capriciously, on the cuprous oxide specimens used in the pyrolysis. The product was purified by steam distillation and recrystallisation from methanol, m.p. = 110-11°C[8].

The infra-red absorption spectrum showed the absence of biphenyl and the ultra-violet absorption spectrum the same with that previously reported[8] (Table 3.3).



Scheme 3.1

Synthetic routes of biphenylene

Molecular chlorination of biphenylene in acetic acid under heterolytic reaction conditions gives low yields of substitution products, of which the only detectable compound is 2-chlorobiphenylene (20% yield)* (IX). The major products result from addition to the hydrocarbon system in which the carbon skeleton appears to be unbroken.

Biphenylene is planar[9] and may be regarded as a "planar biphenyl" structure or as an aromatic hydrocarbon in its own right. In contrast to fluorene[10], biphenylene shows considerable evidence of conjugation across the entire system, so that the diacetylation and dipropionylation[11] of biphenylene under Friedel-Crafts conditions yield mainly 2,6-isomers, with only small amounts of the 2,7-di-substituted derivatives (see chapter 2, page 33).

Biphenylene undergoes electrophilic substitution to give the 2-substituted derivatives[1],[8] in agreement with theoretical prediction.

Halogenation of some biphenylene derivatives occur with ring-opening; thus, 2-methoxy-3-bromobiphenylene[6] and 1,2,3,6,7,8-hexamethoxybiphenylene[12] both give derivatives of 2,2'-dibromobiphenyl as well as the expected bromo-substituted biphenylene (see pages 40 and 76).

In the presence of light, bromination and chlorination of the parent hydrocarbon yields derivatives of 3,8-dibromo-benzocyclooctatetraene (II, X = Br) as well as a small amount of 2-bromobiphenylene (I, X_1 = Br, X_2X_3 = H)[4] and 3,5,6,8-tetrabromo-5,6-dihydrobenzocyclooctatetraene in poor yield and another tetrabromide , 1,2,4a,8b-tetrabromo-

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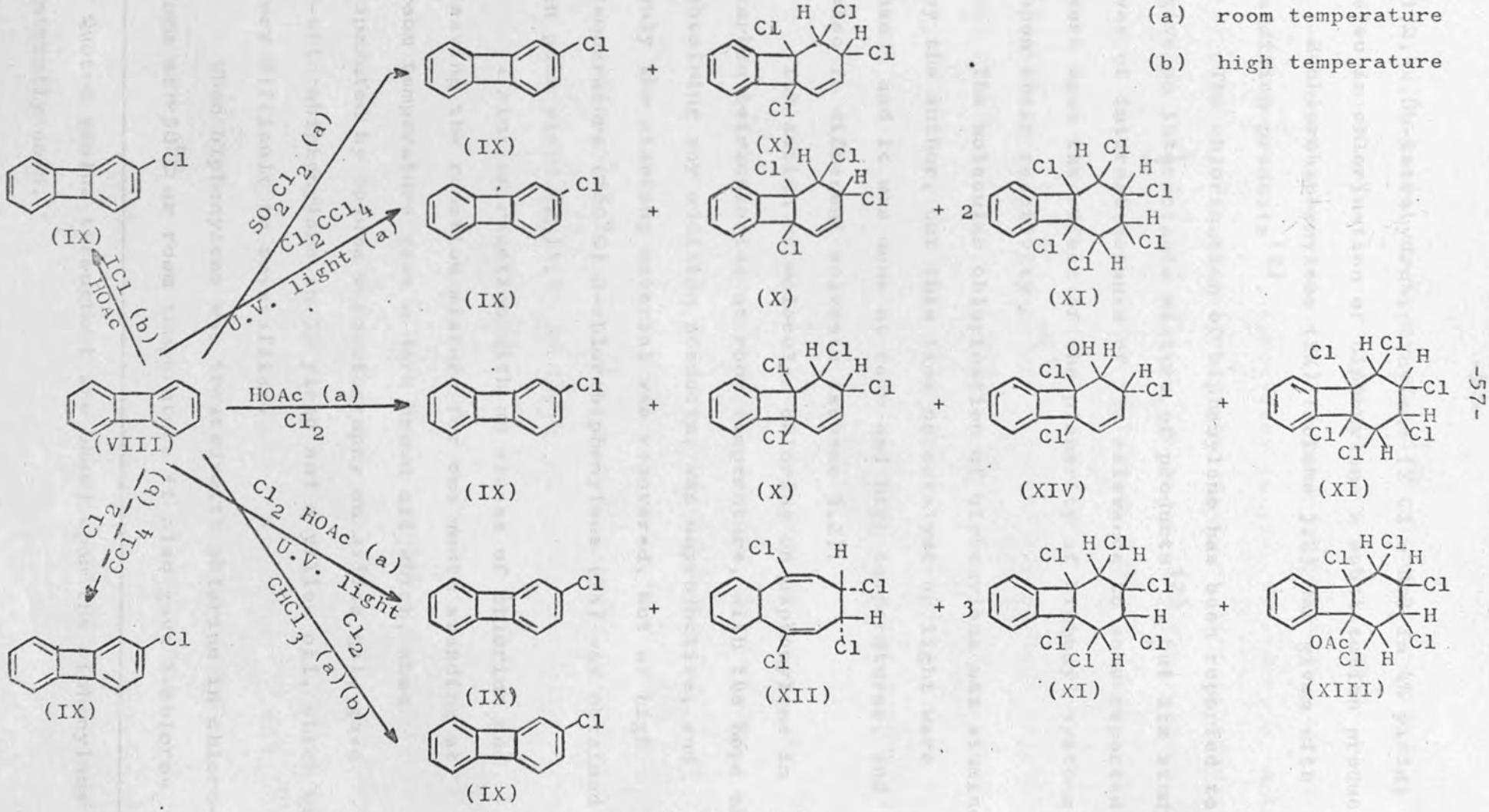
* Quoted yields throughout are based on the biphenylene used initially.



Scheme 3.2

Chlorination of Biphenylene

1,2,4a,8b-tetrahydrobiphenylene (X Cl = Br) in 4% yield; also in chlorination of biphenylene a substitution product, 2-chlorobiphenylene (IX) (scheme 3.2), was given with addition products[2].

The chlorination of biphenylene has been reported to give an interactable mixture of products[2], but its study was of interest because of its relevance to some reported work upon the effect of the planarity of biphenyl systems upon their reactivity.

The molecular chlorination of biphenylene was studied by the author, but this time no catalyst or light were used, and it was done at room and high temperatures, and also in different solvents (scheme 3.2).

The action of molecular chlorine on biphenylene in carbon tetrachloride at room temperature, with the hope of obtaining any addition products, was unproductive, and only the starting material was recovered, but at high temperature (~60°C) 2-chlorobiphenylene (IX) was obtained in poor yield (2%)*.

A similar reaction with an excess of chlorine and leaving the reaction mixture for one month standing at room temperature gave a dark brown oil which, when separated by column chromatography on silica gel, gave 2-chlorobiphenylene in 5% yield and a yellow oil, which was very difficult to crystallise.

When biphenylene was treated with chlorine in chloroform at ~50°C or room temperature it also gave 2-chloro-

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* Quoted yields throughout are based upon the biphenylene initially used.

biphenylene (IX) in 5% yield and 3% yield respectively*, and also colourless oily fractions were found which also, again, were very difficult to obtain as crystals.

Chlorination of biphenylene in glacial acetic acid in the absence of light at room and at higher temperatures was repeated by the author. Again, at room temperature, a complex mixture was given, which on careful chromatography on a silica gel column gave, this time, two crystalline addition products after the unreacted biphenylene (VIII) and 2-chlorobiphenylene (IX) in 20% yield* (see appendix, page 142 (2-chlorobiphenylene was identified by its U.V. and I.R. spectra and its 2,4,7-trinitrofluorenone complex) fractions were taken.

The first fraction was a tetrachloride adduct (X) which was obtained in 2.5% yield, and its ultra-violet (Table 3.2) and N.M.R. spectra (Table 3.3 and Fig. 3.3) have great similarity with those of tetrabromide[4] and identical with those of the compound prepared by Whitaker[2], so this compound is to be 1,2,4a,8b-tetrachloro-1,2,4a,8b-tetrahydrobiphenylene (X).

The second component isolated by chromatography was a hydroxytrichloride (XIV), the infra-red (Fig. 3.2) and the N.M.R. spectra (Table 3.3 and Fig. 3.4) of which shows (-OH) group and whose N.M.R. spectrum again showed a great similarity with that of the known tetrabromide[4] and tetrachloride[2], 1,2,4a,8b-tetrahydrobiphenylenes.

When the hydroxytrichloride (XIV) was treated with

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* Quoted yields throughout are based upon the biphenylene initially used.

TABLE 3.2

Ultra-violet Absorption Characteristics of Addition Products of Biphenylene*

Biphenylene	Absorption maxima, mμ, and extinction coefficient (log ε)
Tetrabromide[4]	207(4.36); 217(4.34); 278(3.58); 254(3.58)
Tetrachloride	209(4.29); 221(4.01); 263(3.02); 270(3.22); 277(3.12)
Tetrachloride[2]	209(4.33); 220(4.03); 263.5(3.01); 270(3.21); 276.5(3.17)
Trichlorohydroxy-	255°(3.08); 261(3.13); 276(3.16); 274(3.09); 295°(2.35); 305(2.24)

* All spectra determined in 95% ethanol

° Shoulder or an inflection

TABLE 3.3

Nuclear Magnetic Resonance of some Addition Compounds of Biphenylene*

Compounds	Tetra-chloride(2)	Tetra-chloride	Tetra-bromide(4)	Hydroxy-trichloride
Spectrum type	AB	AB	AB	AB
(p.p.m.)				
Aromatic (H_{5-8})	2.33 - 2.95	2.20 - 2.85	2.30 - 3.04	2.23 - 2.95
-OH				6.39
1-H	5.66	5.50	5.40	5.60
2-H	6.08	5.95	5.83	6.04
3-H	3.70	3.57	3.61	3.71
4-H	4.26	4.14	4.23	4.20
Coupling constants (c sec^{-1}):				
$J_{1,2}$	10.00	10.00	9.70	10.40
$J_{2,3}$	2.50	2.40	2.30	2.40
$J_{3,4}$	10.60	10.20	10.20	10.30
$J_{2,4}$	1.60	1.60	1.90	1.40

* Deuterochloroform as solvent.

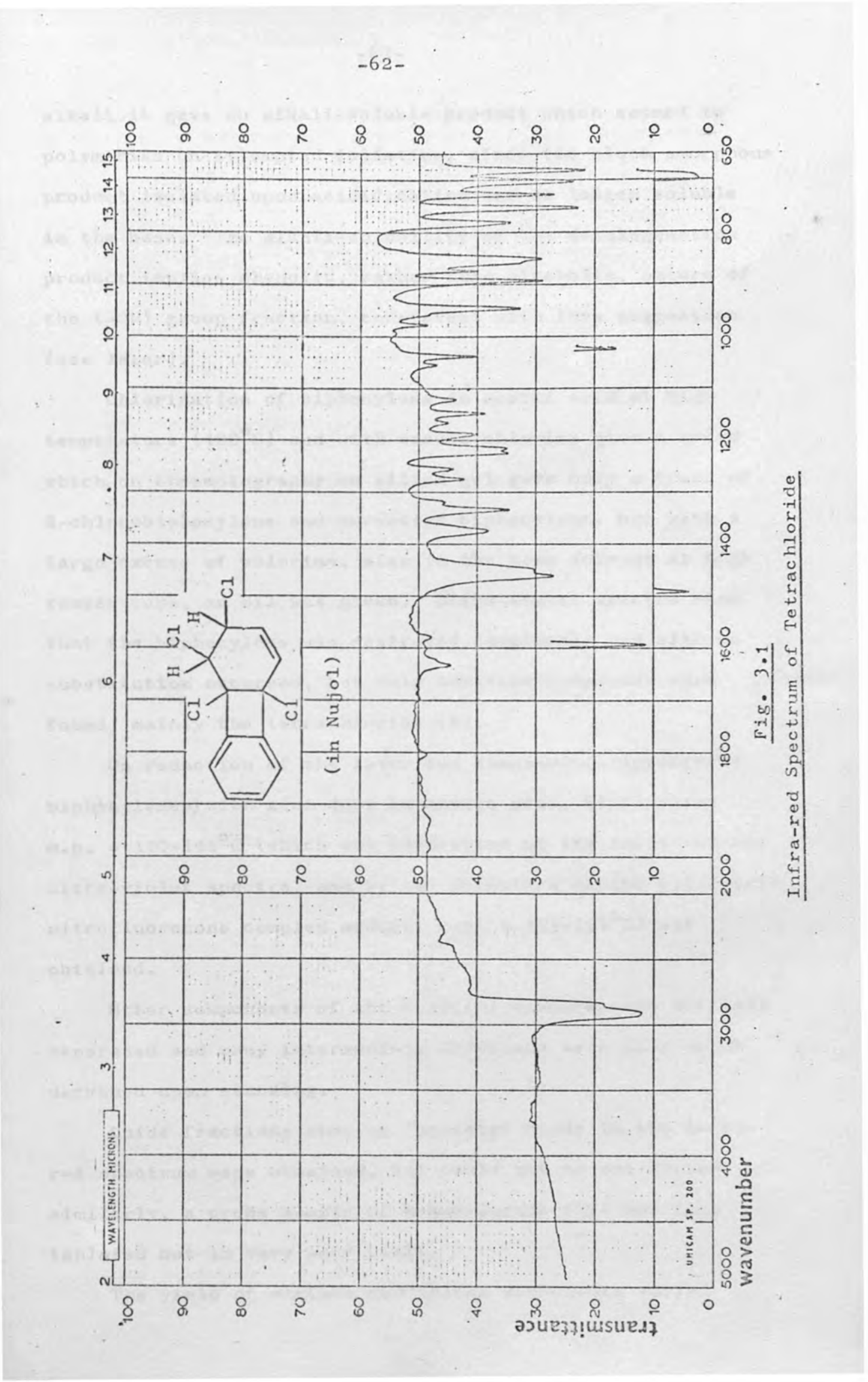


Fig. 3.1

Infra-red Spectrum of Tetrachloride

alkali it gave an alkali-soluble product which seemed to polymerise on attempted isolation, since the black amorphous product isolated upon acidification was no longer soluble in the base. The alkali-solubility of the dehalogenation product implies phenolic, rather than alcoholic, nature of the (-OH) group fraction, consistent with this suggestion (see later).

Chlorination of biphenylene in acetic acid at high temperature (100°C) and with excess chlorine gave a solid which, on chromatography on silica gel gave only a trace of 2-chlorobiphenylene and unreacted biphenylene, but with a large excess of chlorine, also in the same solvent at high temperature, an oil was given. Ultra-violet spectra show that the biphenylene was destroyed completely and also no substitution occurred, but only addition compounds were found, mainly the tetrachloride (X).

On reduction of the later two compounds (chlorohydrobiphenylenes) with zinc dust in acetic acid, biphenylene m.p. = 110-111°C (which was identified by its infra-red and ultra-violet spectra, and by the formation of the 2,4,7-trinitrofluorenone complex adduct, m.p. = 153-154°C) was obtained.

Other components of the reaction mixture were not well separated and many intermediate fractions were oils which darkened upon standing.

Guide fractions showing "acetate" bands in the infra-red spectrum were obtained, but could not be solidified; similarly, a crude sample of hexachloride (XI) was also isolated but in very poor yield.

The yield of various conditions components varied

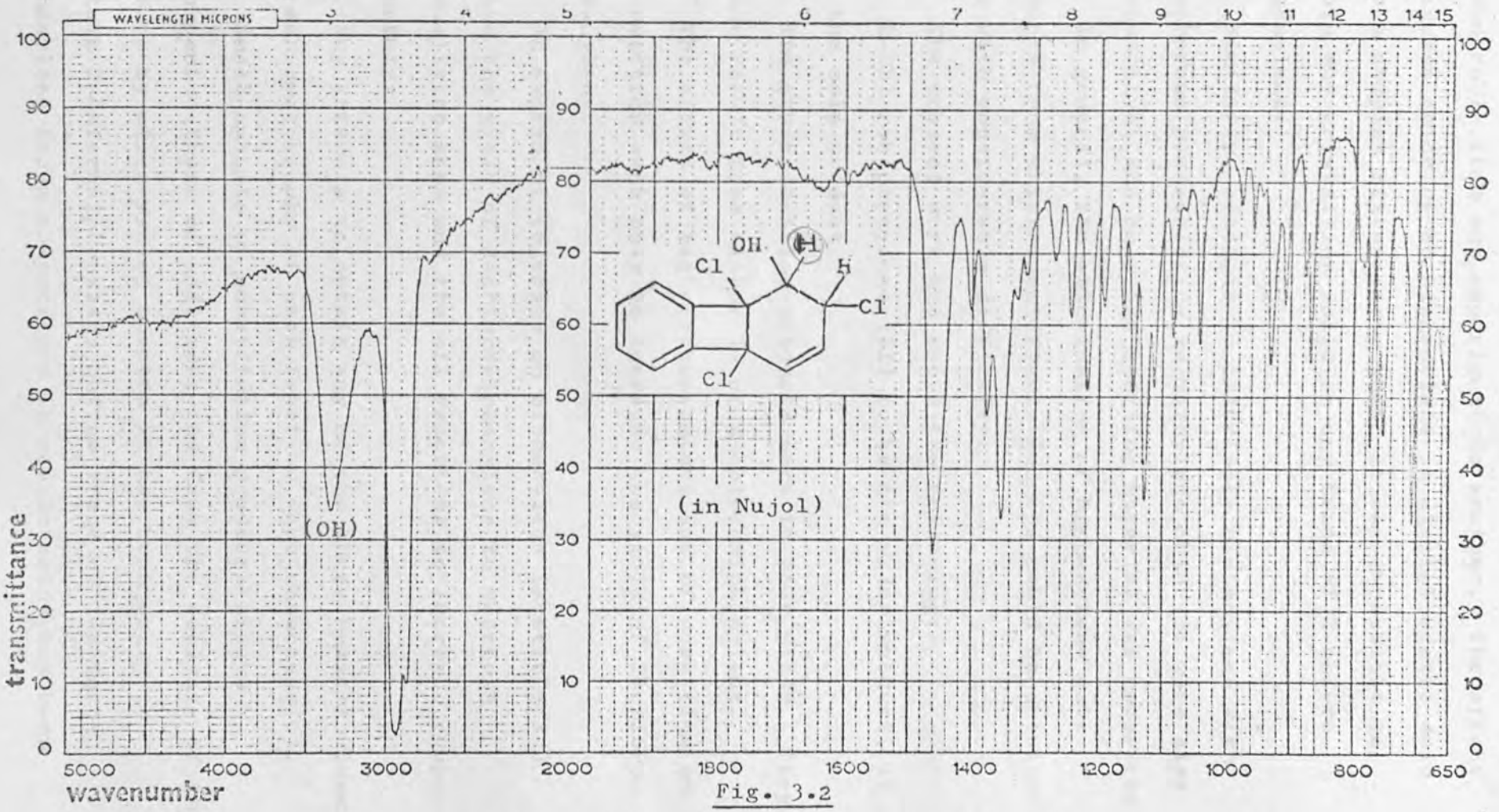


Fig. 3.2

Infra-red Spectrum of Hydroxytrichloride

considerable from one experiment to another. The effect of excess chlorine on biphenylene in glacial acetic acid gave a complex mixture from which it was impossible to obtain any crystalline solid or any trace of 2-chloro-biphenylene.

Similarly, attempts to chlorinate biphenylene with phosphorous pentachloride in methylene chloride were also unproductive, and only the starting material was recovered.

In general, the chlorination of biphenylene gave products from which identifiable adducts could be obtained only with considerable difficulty.

The present work has shown the following:-

a. 2-Chlorobiphenylene (IX) to be the major product, if not the sole product.

b. The other addition products were in poor yield. They cannot result from either 1- or 2-chlorobiphenylene.

c. The effect of higher temperature and of more time on the reaction were only to increase the yield of 2-chloro-biphenylene.

d. An excess of chlorine on biphenylene (acetic acid) caused the yield of 2-chlorobiphenylene to decrease gradually to zero and the oil fractions to increase proportionately.

e. Any attempts to obtain any of the three hexachlorides[2] by rechromatography of each fraction were unsuccessful.

Small amounts of substitution products always accompanied those of addition, and from the analysis of the mixture by ultra-violet spectra it has been shown to contain 2-chlorobiphenylene but no trace of 1-chloro-biphenylene (room temperature in acetic acid) has been

found, but 1-chlorobiphenylene (chapter 4) was prepared by pyrolysis of 4-chlorobiphenylene iodonium iodide with cuprous oxide at 360°C, which is used here as a reference.

Chlorination of biphenylene in chloroform or carbon tetrachloride at high temperature with excess chlorine gave 2-chlorobiphenylene and from ultra-violet spectra, the reaction mixture contains a trace of 1-chlorobiphenylene. These two chlorinations were under investigation by the author in detail.

Chlorination of biphenylene with sulphuryl chloride in chloroform at room temperature by leaving the reaction mixture standing for ten days, this time gave the substitution product 2-chlorobiphenylene again, followed by the addition product of tetrachloride, which is identical with that prepared before, so this tetrachloride is to be 1,2,4a,8b-tetrachloro-1,2,4a,8b-tetrahydrobiphenylene (X) (scheme 3.2) and again other components of the reaction were not well separated and many intermediate fractions were yellow oils which could not be solidified by leaving to stand for a long time and also the yellow colour of the oils never changed in this time.

Attempts to prepare the dichloride (II, X_1 = Cl) by chlorinating biphenylene with excess of sulphuryl chloride with solvent (nitrobenzene) or without solvent at room temperature or reflux temperature, were unsuccessful and only 2-chlorobiphenylene (IX) and oily fractions were obtained. Also the yield of 2-chlorobiphenylene decreased with increase in the amount of sulphuryl chloride but no trace of 3,8-dichlorobenzocyclooctatetraene (II, X = Cl) was found, but poor yield of tetrachloride was found.

Barton[3] has prepared a dichloride by the action of sulphuryl chloride on biphenylene and he found from the ultra-violet and N.M.R. spectra of this dichloride that it had an expanded ring-opened structure identical with that of dibromide[4].

3.3 The N.M.R. spectra of the addition products

Barton et al[4] and Whitaker[2] have studied the N.M.R. spectra of both tetrabromide and tetrachloride in detail.

1. The Tetrachloride (X)

The non-benzenoid absorption consists of two separated AB systems, with one proton of one system coupled to both protons of the second. This spectra can only show (Fig. 3.3) the structure (X), which involves simple addition to the biphenylene nucleus without ring-opening, so that this tetrachloride must be the tricyclic system, 1,2,4a,8b-tetrachloro-1,2,4a,8b-tetrahydrobiphenylene.

The AB system at midfield is assigned to the two aliphatic protons H^1 and H^2, where H^2 is situated at the highest field and is coupled to both protons, while H^3 and H^4 are both situated at lower field (Fig. 3.3).

The magnitude of this coupling, $J_{2,3}$ and $J_{2,4}$, is different in each case to those of the tetrachloride, which are very similar[4], and this should explain why the fine splitting of H^2 consists of two definite quartets.

The olefinic proton at lowest field is assigned to H^3 rather than H^4, as it has the larger coupling constant with H^2, i.e. $J_{2,3}$ is larger than $J_{2,4}$ (Table 3.3). Since the coupling constant ($J_{1,2}$ = 10.0c/sec) between the protons

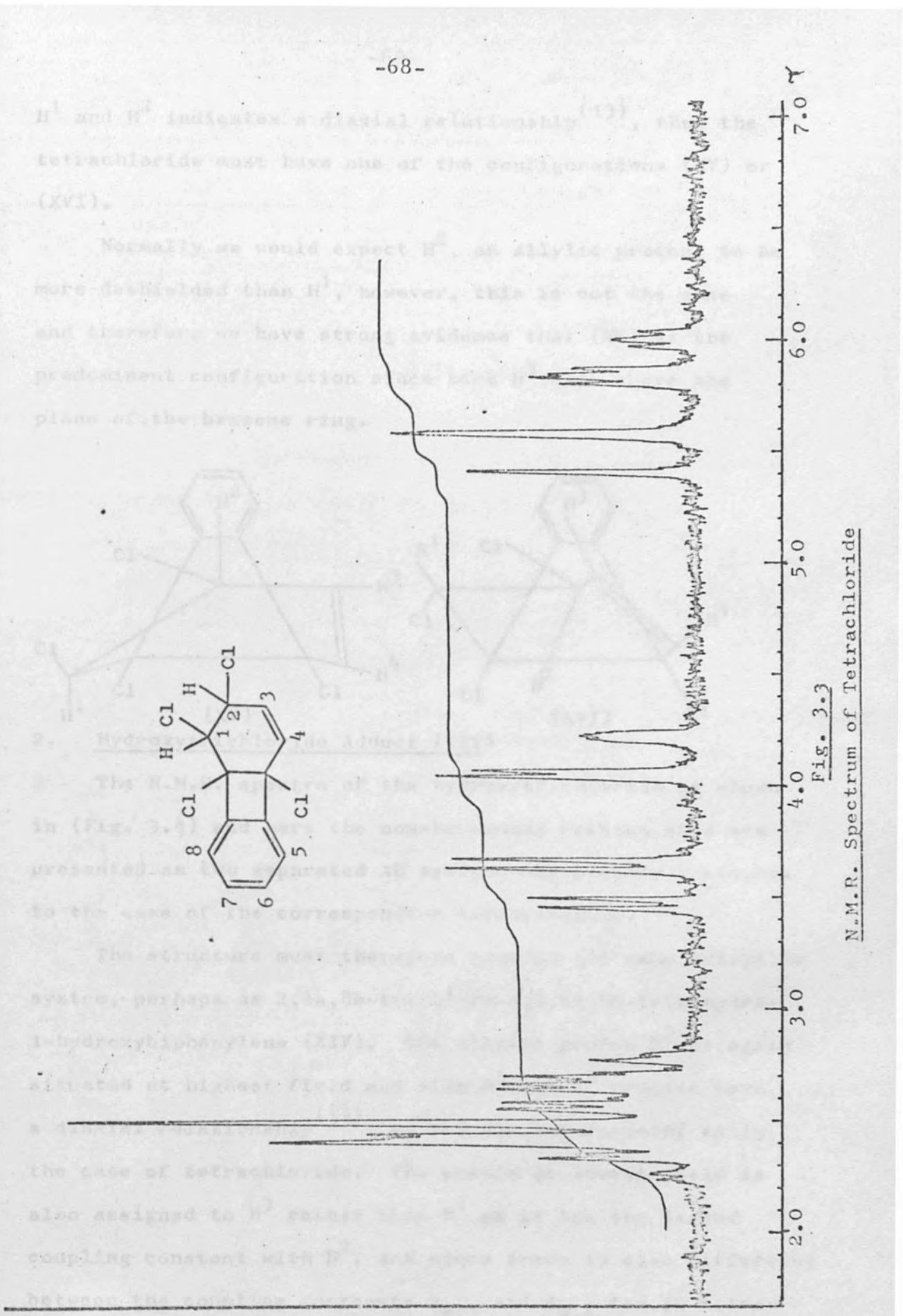
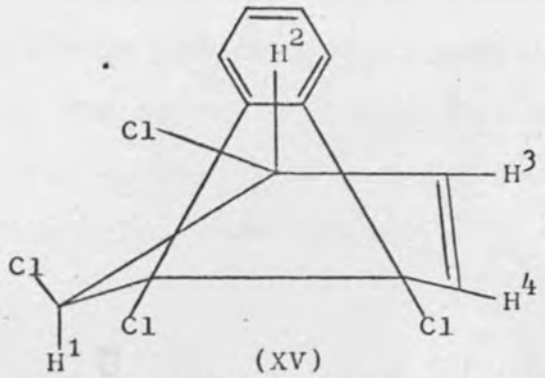


Fig. 3.3

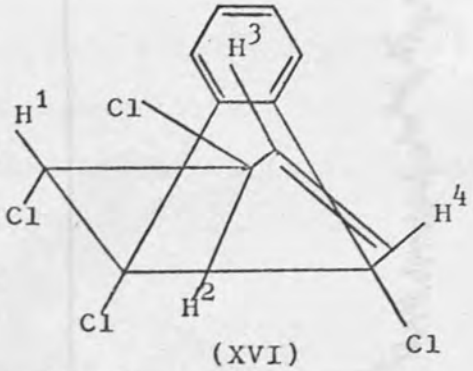
N.M.R. Spectrum of Tetrachloride

H^1 and H^2 indicates a diaxial relationship[13], then the tetrachloride must have one of the configurations (XV) or (XVI).

Normally we would expect H^2, an allylic proton, to be more deshielded than H^1, however, this is not the case and therefore we have strong evidence that (XV) is the predominent configuration since here H^3 lies above the plane of the benzene ring.



(XV)



(XVI)

2. Hydroxytrichloride Adduct (XIV)

The N.M.R. spectra of the hydroxytrichloride is shown in (Fig. 3.4) and here the non-benzenoid protons also are presented as two separated AB systems and closely analogous to the case of the corresponding tetrachloride.

The structure must therefore contain the same tricyclic system, perhaps as 2,4a,8b-trichloro-1,2,4a,8b-tetrahydro-1-hydroxybiphenylene (XIV). The allylic proton H^2 is again situated at highest field and also H^1 and H^2 protons have a diaxial relationship[13], by the similar resuming as in the case of tetrachloride. The proton at lowest field is also assigned to H^3 rather than H^4 as it has the larger coupling constant with H^2, and since there is also difference between the coupling constants $J_{2,3}$ and $J_{2,4}$ (as in tetrachloride) so the fine structure of H^2 consists of two

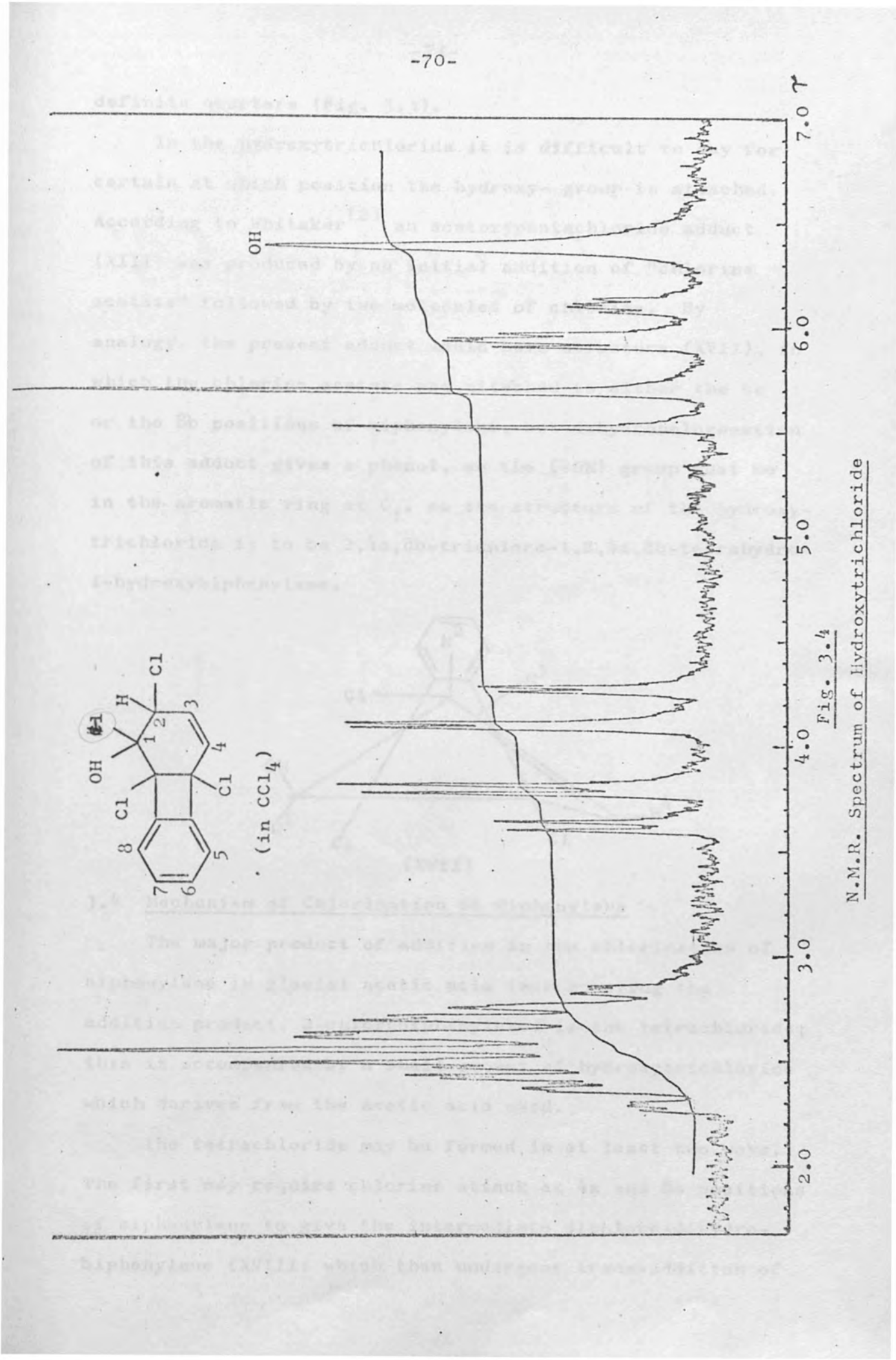
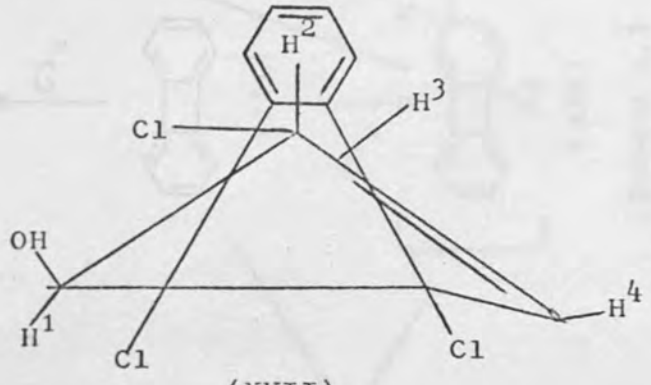


Fig. 3.4

N.M.R. Spectrum of Hydroxytrichloride

definite quarters (Fig. 3.3).

In the hydroxytrichloride it is difficult to say for certain at which position the hydroxy- group is attached. According to Whitaker[2] an acetoxypentachloride adduct (XIII) was produced by an initial addition of "chlorine acetate" followed by two molecules of chlorine. By analogy, the present adduct would have structure (XVII), in which the chlorine acetate was attached to either the 4a or the 8b positions of biphenylene, but dehydrohalogenation of this adduct gives a phenol, so the (-OH) group must be in the aromatic ring at C_1, so the structure of the hydroxy-trichloride is to be 2,4a,8b-trichloro-1,2,4a,8b-tetrahydro-1-hydroxybiphenylene.

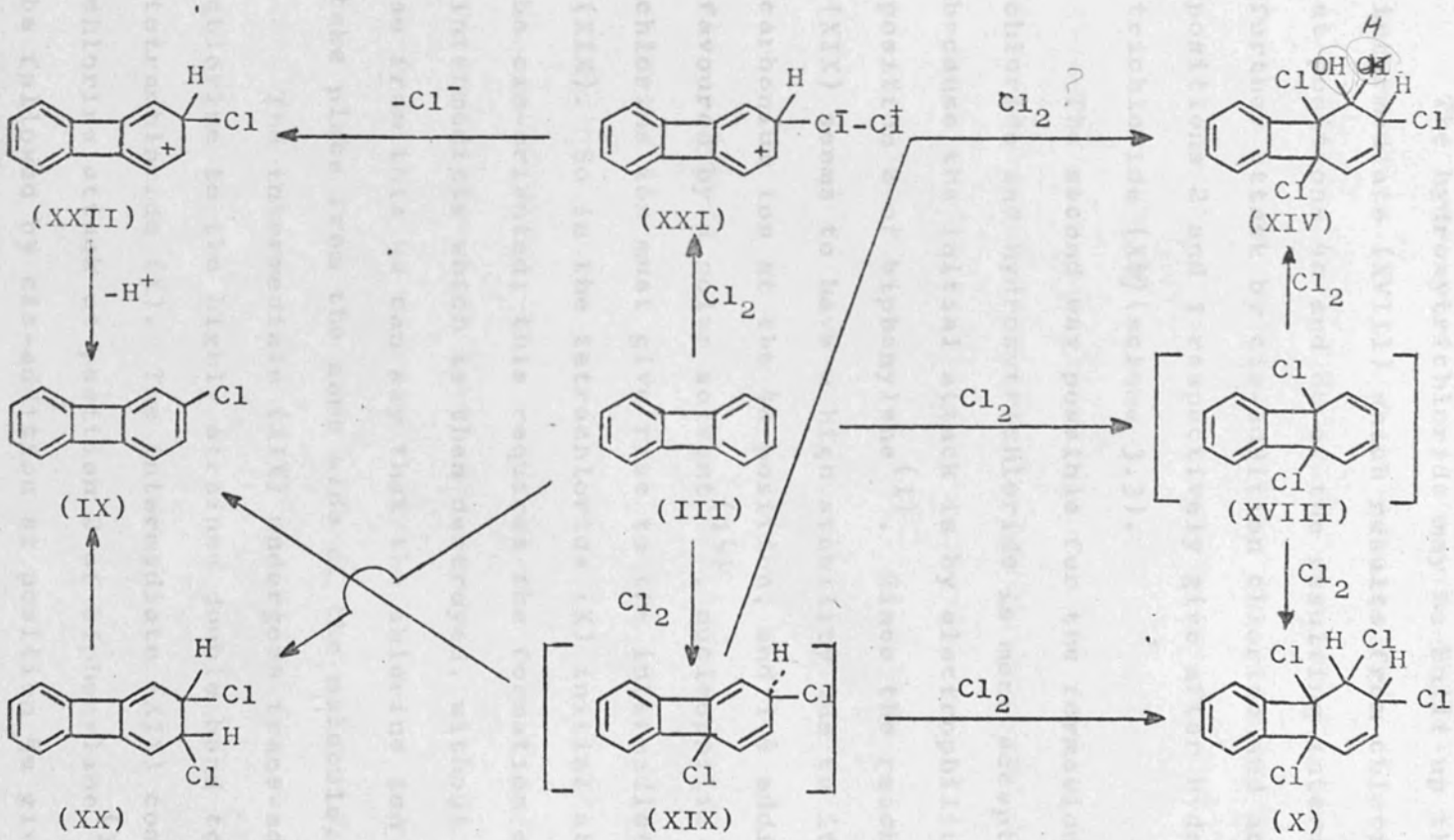


(XVII)

3.4 Mechanism of Chlorination of Biphenylene

The major product of addition in the chlorination of biphenylene in glacial acetic acid (accompanying the addition product, 2-chlorobiphenylene) is the tetrachloride; this is accompanied by a small amount of hydroxytrichloride which derives from the acetic acid used.

The tetrachloride may be formed in at least two ways. The first may require chlorine attack at 4a and 8b positions of biphenylene to give the intermediate dichloro-dihydro-biphenylene (XVIII) which then undergoes trans-addition of



Scheme 3.3

Mechanism of Chlorination of Biphenylene

chlorine to one of the remaining double bonds to obtain a tetrachloride (X).

The hydroxytrichloride may be built up through the intermediate (XVIII) which results from chlorine attack at positions 4a and 8b of the resulting intermediate; further attack by cis-addition chlorine and acetate at positions 2 and 1 respectively give after hydrolysis hydroxytrichloride (XIV) (scheme 3.3).

The second way possible for the formation of tetrachloride and hydroxytrichloride is more acceptable because the initial attack is by electrophilic chlorine at position 2 of biphenylene[1]. Since the resonance form (XIX) seems to have a high stability due to its benzylic carbonium ion at the 4a position, and 1,4 addition is favoured by a polar solvent[14], nucleophilic attack by chlorine ion must give rise to the intermediate dichloride (XIX). So in the tetrachloride (X) initial attack should be cis-oriented; this requires the formation of an ion-pair intermediate which is then destroyed, without rearrangement, so from this we can say that the chlorine ion attack can take place from the same side of the molecule.

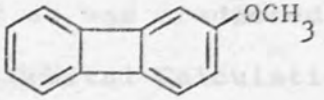
The intermediate (XIX) undergoes trans-addition of chlorine to the highly strained double bond to give a tetrachloride (X). The intermediate (XIX) comes from chlorine attack at position 2 of biphenylene[1] which may be followed by cis-addition at position 4a giving the intermediate (XIX) rather than proton elimination to give 2-chlorobiphenylene (IX), the normal substitution product. Then further cis-addition of the more strained double bonds will form tetrachloride or the hydroxytrichloride

(XIV), depending upon which nucleophile (Cl^- or AcO^-) is incorporated in the second stage of the addition.

The product of substitution, 2-chlorobiphenylene, may be formed in two other ways; first from the intermediate (XX) 1,2-dichloro-1,2-dihydrobiphenylene which then may lose hydrogen chloride to form the product of substitution, and secondly, from the carbonium intermediate (XXI) which by losing chlorine ion to form the intermediate 2-chloro-hydrobiphenylene carbonium ion (XXII) which also gives 2-chlorobiphenylene (IX) by losing hydrogen ion.

The difference between the two ways of the formation of addition products is that in the first way, the intermediate (XVIII) with further chlorine gave tetrachloride or hydroxytrichloride but perhaps no substitution product. This intermediate is not likely because no dichloro-compound (II, X = Cl) was obtained in direct chlorination of biphenylene (Barton[3] prepared it by the action of sulphuryl chloride on biphenylene) because of the rapid chlorine attack at positions 4a and 8b, while in the second path the chlorine attack at both positions 2 and 4a of biphenylene may give 2-chlorobiphenylene and then more attack of chlorine to give the tetrachloride or hydroxy-trichloride.

CHLORINATION OF 2-METHOXYBIPHENYLENE



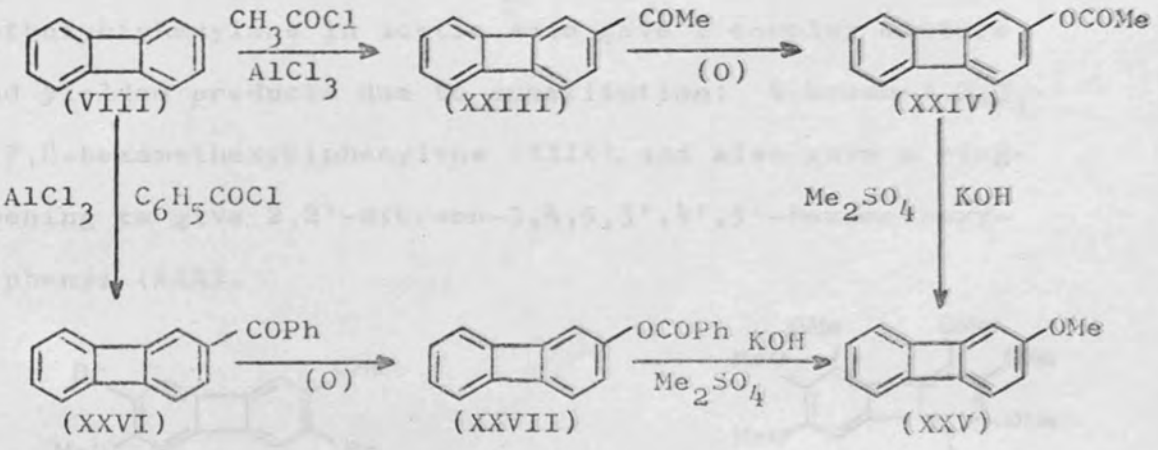
(XXV)

3.5 Preparation of 2-Methoxybiphenylene

2-Methoxybiphenylene can be prepared by Lothrop's method. Baker et al[15] have prepared this compound by pyrolysis of 3-methoxybiphenylene iodonium iodide with cuprous oxide at 360°C in 8% yield (see chapter 2).

Later, Blatchly et al[5] prepared it by oxidation of 2-acetylbiphenylene (XXIII) with peracetic acid to obtain 2-acetoxybiphenylene (XXIV) which on combined hydrolysis and methylation gave 2-methoxybiphenylene (XXV in 81% yield.

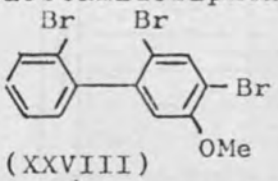
We have prepared 2-methoxybiphenylene by oxidation of 2-benzoylbiphenylene (XXVI)[16] with peracetic acid to give 2-benzoyloxybiphenylene (XXVII) the latter being converted into 2-methoxybiphenylene also by combined hydrolysis and methylation in 90% yield.



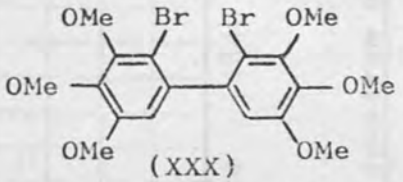
3.6 Chlorination of 2-Methoxybiphenylene

Biphenylene has been shown[1] to undergo electrophilic substitution at position 2 as was predicted by Brown on the basis of Molecular Orbital Calculations.

The position at which further electrophilic attack occurs is governed by the type of substituent already present. So we know that the methoxy- group is an ortho-para directing group which is present at position 2 of biphenylene. Substitution will occur at adjacent position 3 according to Longuet-Higgins[17] on the basis of the Molecular Orbital Theory, but it has been shown that mono-substitution of 2-methoxybiphenylene (XXV) occurs at the 3-position when it reacts with molecular bromine at room temperature to give 2-methoxy-3-bromobiphenylene, which with more bromine gave a ring-opening to give 2,2',4-tribromo-5-methoxy-biphenyl[6] (XXVIII), behaviour which is also similar to that of 2-acetamidobiphenylene.

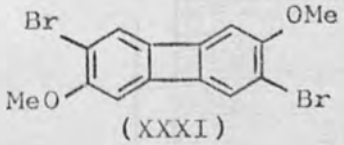


(XXVIII)

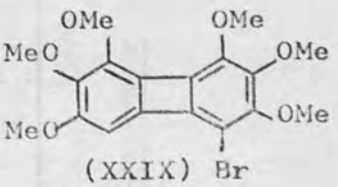


(XXX)

Bromination of polymethoxybiphenylenes so far recorded deals with 1,2,3,6,7,8-hexamethoxybiphenylene[12] and 2,6- and 2,7-dimethoxybiphenylenes; bromination of hexa-methoxybiphenylene in acetic acid gave a complex mixture and yielded products due to substitution; 4-bromo-1,2,3,-6,7,8-hexamethoxybiphenylene (XXIX), and also gave a ring-opening to give 2,2'-dibromo-3,4,5,3',4',5'-hexamethoxy-biphenyl (XXX).



(XXXI)



(XXIX) Br

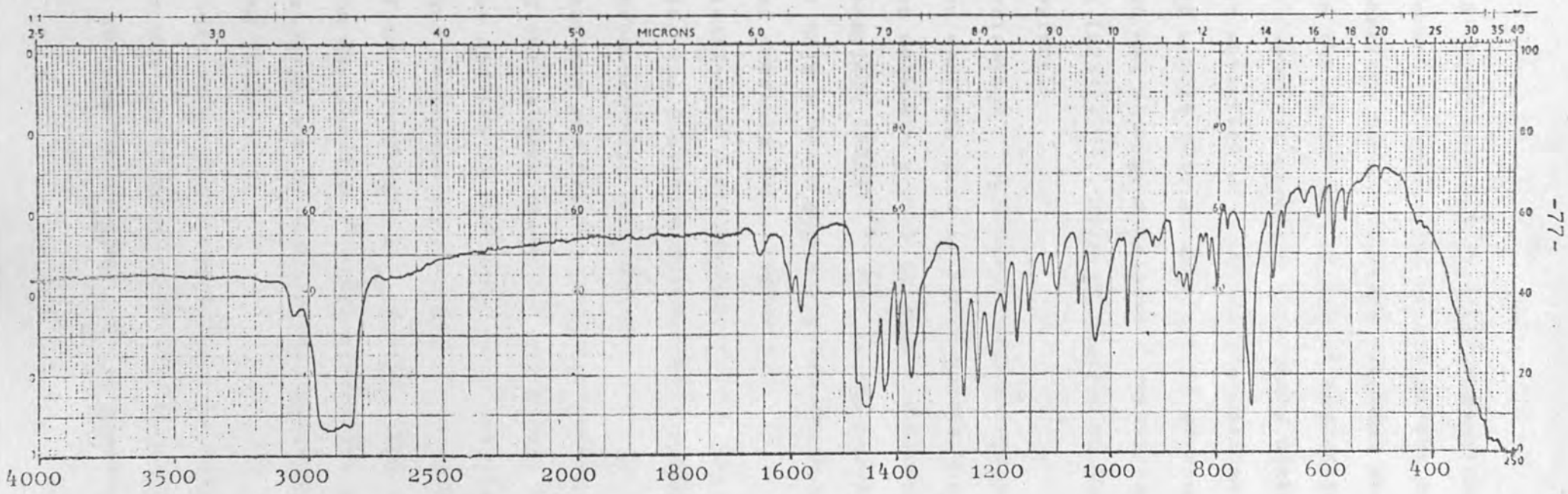


Fig. 3.5

Infra-red Spectrum of 2-Methoxy-3-chlorobiphenylene

The 2,2'-dibromo-3,4,5,3',4',5'-hexamethoxybiphenyl (XXX) was formed by bromolysis of one of the central bonds of the biphenylene structure; this reaction was exactly analogous to the conversion of parent biphenylene into biphenyl by reductive cleavage with Raney nickel

Also in nitration of 2-methoxybiphenylene with concentrated nitric acid in acetic acid at room temperature substitution was undergone to give 2-methoxy-3-nitrobiphenylene (XXXII)[6]. This is similar to that of 2-acetamidobiphenylene.

In bromination of 2,6-dimethoxybiphenylene also substitution was undergone at the β-position adjacent to both the two methoxy- groups to give 2,6-dimethoxy-3,7-dibromobiphenylene (XXXI)[6] but in chlorination of this biphenylene only a black gum was given which was impossible to obtain as crystals (see chapter 5).

Chlorination of 2-methoxybiphenylene has also been found to give the 2-methoxy-3-chlorobiphenylene, by analogy with that bromomethoxy- derivatives, but when 2-methoxy-3-chlorobiphenylene was chlorinated with excess chlorine in acetic acid only a dark brown oil was given, and from ultra-violet spectra it has been shown that the biphenylene structure was destroyed completely, maybe to biphenyl; this oil is difficult to obtain as crystals. The two monosubstitution derivatives of biphenylene have almost identical absorptions in ultra-violet spectra (Fig. 3.6 and Fig. 3.7 and Table 3.3).

Chlorination of 2-methoxybiphenylene with sulphuryl chloride in boiling chloroform or nitrobenzene on standing for a week at room temperature gave no reaction and only

Table 3.3

Ultra-violet Absorption Characteristics of Biphenylene Derivatives*

Biphenylene	Absorption maxima, mμ, and extinction coefficient (log ε)
Biphenylene[8]	239(4.77); 248(5.05); 326(3.47); 330(3.49); 339(3.79); 343(3.76); 348(3.58); 358(3.97).
Biphenylene	239.5(4.78); 248(5.07); 326(3.41); 330(3.44); 338.7(3.74); 343(3.71); 348.4(3.52); 357.8(3.92).
2-Methoxy-3-chloro-	248(3.89); 255(4.05); 354(3.13); 372(3.25).
2-Methoxy-3-bromo-	248.5(3.47); 256(4.03); 353(3.18); 372(3.33).
2-Nitro-6-chloro- (Whitaker)	235.5(4.34); 241.5(4.36); 246(3.44); 265(4.45); 363(3.65); 394(3.49).
2-Nitro-6-chloro-	235(4.27); 241(4.30); 245(3.39); 265(4.40); 364(3.60); 394(3.42).

* All the spectra determined in 95% ethanol.

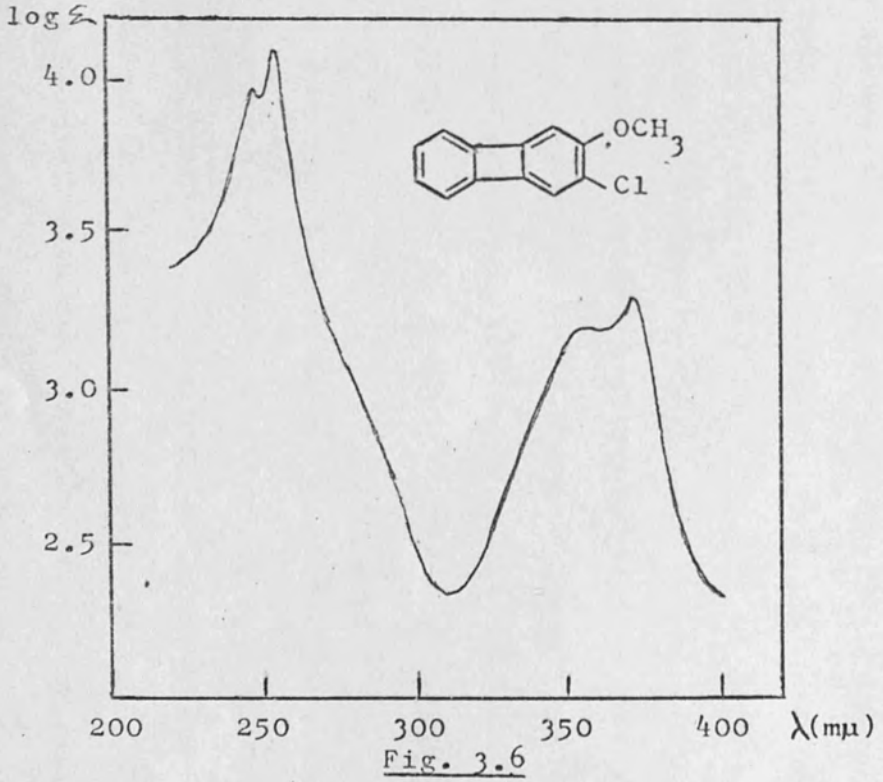


Fig. 3.6

Ultra-violet Absorption of

2-methoxy-3-chlorobiphenylene in 95% ethanol

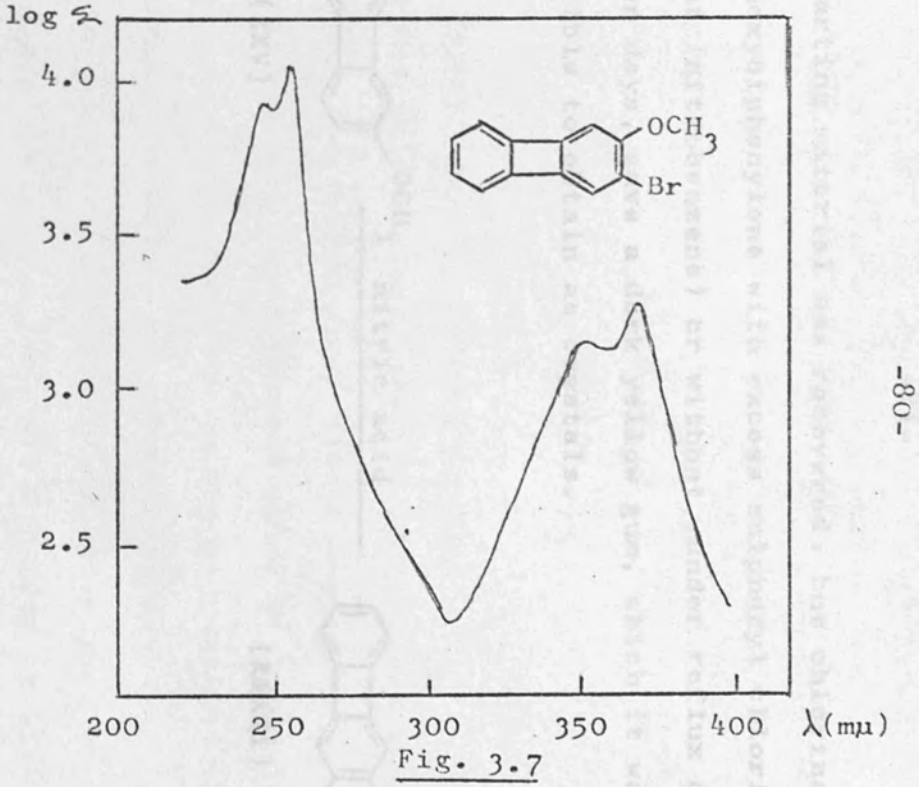
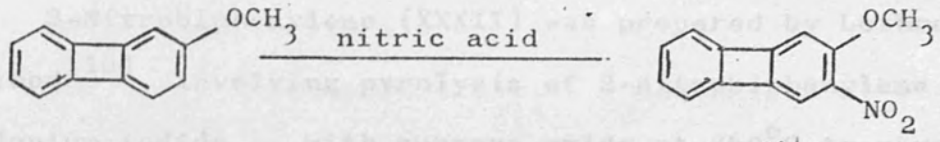


Fig. 3.7

Ultra-violet Absorption of

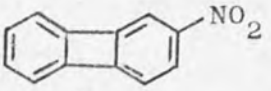
2-methoxy-3-bromobiphenylene in 95% ethanol

the starting material was recovered, but chlorination of 2-methoxybiphenylene with excess sulphuryl chloride, with solvent (nitrobenzene) or without, under reflux or standing for ten days, gave a dark yellow gum, which it was impossible to obtain as crystals.



(XXV) (XXXII)

CHLORINATION OF 2-NITROBIPHENYLENE



(XXXII)

3.7 Preparation of 2-Nitrobiphenylene

2-Nitrobiphenylene (XXXII) was prepared by Lothrop's method[16], involving pyrolysis of 2-nitrobiphenylene iodonium iodide with cuprous oxide at 360°C to give, in poor yield, the biphenylene which was purified by steam distillation to obtain pure 2-nitrobiphenylene (XXXII).

The nitration of biphenylene under various conditions gives a mixture of 2-nitro- and a little of 2,6-dinitro-biphenylenes but by adjusting conditions (acetic acid and acetic anhydride at 0°C) it gave 2-nitrobiphenylene in 23.5% yield (nitration of biphenylene with concentrated nitric acid and sulphuric acid gave a mixture of 2-nitro- and 2,6-dinitrobiphenylene).

The orientation of 2-nitrobiphenylene (XXXII) was confirmed by reducing it to 2-aminobiphenylene which had already been prepared from 2-acetylbiphenylene.

The reactivity of 2-nitrobiphenylene shows that the nitro- group has controlled all other positions in biphenylene and that position 6 must be the more reactive to attack than position 7, so that chlorination of 2-nitrobiphenylene we expected to give 2-nitro-6-chlorobiphenylene (XXXIII). Formation of the 2-nitro-7-chlorobiphenylene (XXXIV) isomer would be unfavourable since the nitro- group would deactivate electrophilic substitution at this point.

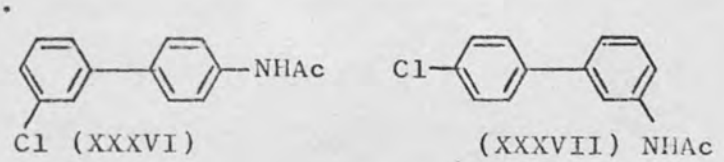
Nitration of 2-chlorobiphenylene must give a mixture

of 2-chloro-6-nitrobiphenylene and 2-chloro-6,7-dinitrobiphenylene; these two isomers compounds are very difficult to separate.

3.8 Chlorination of 2-Nitrobiphenylene

Chlorination of 2-substituted biphenylenes has been studied very little because of its great difficulty and because of the complex mixture of products.

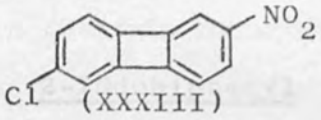
Whitaker[2] has reported that chlorination of 2-nitrobiphenylene in glacial acetic acid on irradiation with U.V. light to give a mono-chloronitrobiphenylene in poor yield (16%) and colourless compound, as nitroacetoxypentachloride adduct (XXXV). The structure of the chloronitrobiphenylene was proved by N.M.R. measurements and by reducing the nitro- group to amino- group which was then removed by diazotisation to give 2-chlorobiphenylene (IX). The latter 2-chlorobiphenylene was conclusive evidence for the B-position of the chlorine atom in the original chloronitrobiphenylene (6 or 7 position), and also the amino-group could be acetylated to give 2-acetamido-6-chlorobiphenylene which then reduced to give two isomers (XXXVI) and (XXXVII).



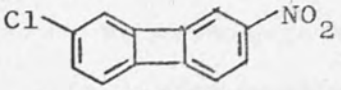
(XXXVI) (XXXVII)

Whitaker[2] prepared 4-acetamido-4'-chlorobiphenyl and compared the ultra-violet spectrum of this biphenyl with that of the reduction of 2-acetamido-6-chlorobiphenylene. He found that the 4-amino-4'-chlorobiphenyl is not present as one of the Raney nickel cleavage products, so the original

biphenylene is to be 2-nitro-6-chlorobiphenylene (XXXIII). The 2,7- analogue would be expected to give 4-chloro-4'-acetamidobiphenyl along the 3,3'-isomeric.

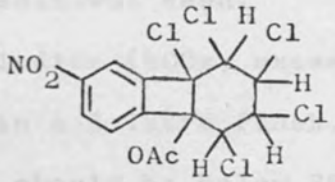


(XXXIII)



(XXXIV)

We have repeated this reaction in the absence of light and at room temperature giving a solid which was separated by column chromatography on silica gel. The first fractions gave a solid which crystallised from methanol as deep yellow needles, m.p. = 189-190°C. This biphenylene (2.5% yield) was identical with that prepared by Whitaker in its ultra-violet spectrum (Table 3.1) and in the identity of melting points, and was therefore 2-nitro-6-chloro-biphenylene. The second fractions were unreacted 2-nitro-biphenylene, but no trace of 2-nitroacetoxypentachloride adduct product was found.



(XXXV)

3.9 Experimental Section

Preparation of Biphenylene

1. 2-Iodobiphenyl

2-Aminobiphenyl (170g, 1 mole) was suspended in hot water (300 ml) in a 1.5 litre flask, and the oily suspension was stirred vigorously. Hydrochloric acid (36%, 12N, 260 ml) was added slowly so that the amine hydrochloride was formed as completely as possible.

The reaction mixture was now cooled as quickly as possible to obtain small crystals of 2-aminobiphenyl hydrochloride and it was held at 0 - 5°C (ice/salt bath) while sodium nitrite (72g) in water (150 ml) was added to diazotise the amine. After all the nitrite was added the suspension was stirred for at least half an hour at 5°C or until no solid salt was seen.

Potassium iodide (400g, excess) was dissolved in hot water (500 ml) in a 5 litre flask. (The final temperature of the solution should be below 25°C). The diazonium solution was then slowly added to the iodide solution, allowing each evolution of nitrogen to occur before adding fresh reagent.

Finally the reaction mixture was heated on a boiling water bath until no further evolution of nitrogen occurred. The iodine colour was discharged using sodium metabisulphite, and the lower layer of 2-iodobiphenyl was separated off and washed with water, 2N sodium hydroxide, water again and then dried. The 2-iodobiphenyl was distilled under reduced pressure, using an oil bath and an oil pump (b.p. = 133°/2 mm.,

158°/6 mm.), (200-240g, 71-85%).

2. Biphenylene iodonium bisulphate

Acetic anhydride (1 litre) was treated with sulphuric acid (36N, 5 ml) and vigorously stirred with external cooling while hydrogen peroxide (30%, 200 ml) was added slowly at 20-25°C (care should be taken to allow the heat of reaction to develop and dissipate before adding more peroxide, otherwise a violent reaction will occur). This takes about two hours.

2-Iodobiphenyl (200g) was then added to the solution, which was then treated with more acetic anhydride (200 ml), again keeping the temperature below 25°C. After being left overnight the mixture was stirred while sulphuric acid (200 ml, 18M) was added slowly at 20°C and the mixture was stirred at room temperature for six hours.

The dark product was filtered off through a glass funnel to give a solid which was washed with acetic acid, with water many times and finally with ether and dried. The biphenylene iodonium bisulphate (195g) is an off-white coloured solid.

3. Biphenylene iodonium iodide

Biphenylene iodonium bisulphate (60-70g) was dissolved in boiling distilled water (2 litres). The clear solution was then treated with a solution of an equal weight of potassium iodide, and allowed to cool to about 40°C. The solution was then filtered, and the precipitate was washed several times with water, and then with ether. Biphenylene iodonium iodide (95-100% yield) was obtained as a cream

coloured solid.

4. Biphenylene

Biphenylene iodonium iodide (15g) and copper powder (60g) were mixed together in a flask with an air condenser and placed in a metal bath at 300°C.

On slowly turning the flask and condenser, and then raising the temperature of the bath to 350°C, biphenylene distilled out into the condenser, which was held at an angle to prevent return of the hydrocarbon to the reaction mixture. From time to time the solid in the condenser was removed by stopping the reaction, removing the condenser from the cooled flask, and washing the solid with acetone.

This process was repeated twice with further amounts of biphenylene iodonium iodide, and using the same flask and copper powder.

The yield of biphenylene was between 60 and 70%. Since 2,2'-diiodobiphenyl is also formed in the reaction, and may also be distilled out under these conditions, it is essential to steam distil the hydrocarbon before crystallisation. Two crystallisations from methanol gave biphenylene as long prisms (needles), pale yellow in colour, m.p. = 109-111°C.

1. Chlorination of biphenylene with molecular chlorine in acetic acid at 25°C

Compounds were characterised wherever possible by melting point, mixed melting point and by comparisons of relevent spectra. Infra-red measurements were made with a Unicam SP200 infra-red spectrophotometer. Ultra-violet

spectra were determined with 95% ethanol as solvent by means of a Unicam SP800 or Perkin-Elmer ultra-violet spectrophotometer. Proton magnetic resonance spectra were determined on a Varian associates 60 Mc/sec. spectrophotometer with carbon tetrachloride as solvent and tetramethylsilane as internal reference.

Isolation of biphenylene tetrachloride from chlorination of biphenylene in acetic acid at 25°C

Preliminary experiments showed that the main components of the chlorination of biphenylene were stable in acetic acid, and could be separated by column chromatography on silica gel.

Biphenylene (9.45g, 6.2 mmole) in acetic acid (50 ml.) was treated with a solution of chlorine (5.0g, 7.04 mmole) in acetic acid (100 ml). When the reaction mixture was complete it was poured into one litre of water and the organic products were collected by extraction with ether (5 x 100 ml), drying over anhydrous sodium sulphate. After evaporating the solvent under reduced pressure gave an oil (6.71g) which is dissolved in light petroleum (40 - 60°C) and separated by column chromatography (24 x 2 cm). The hydrocarbon and its products of substitution were eluted with light petroleum (40 - 60°C) and 10 ml fractions were taken.

The first fractions gave a solid which was recrystallised from aqueous methanol to give a pure sample of 2-chlorobiphenylene as very pale yellow plates, m.p. and mixed m.p. = 66-67°C with a specimen prepared from 2-acetoxymercuribiphenylene; both give a complex when reacted with

2,4,7-trinitrofluorenone as scarlet needles m.p. = 133-134°C.

The second fractions gave a solid which was recrystallised from methanol to give a pure sample of unreacted biphenylene, m.p. = 110-111°C, which is identified by infra-red and ultra-violet spectra, and by the 2,4,7-trinitrofluorenone complex.

The third fractions were also given as a solid which was recrystallised from petroleum ether (40 - 60°C), and this solid was 1,2,4a,8b-tetrachloro-1,2,4a,8b-tetrahydrobiphenylene (0.42g) in the form of colourless plates, m.p. = 101-102°C (Found: C, 49.1%; H, 2.7%; Cl, 48.2%. $C_{12}H_8Cl_4$ requires C, 49.0%; H, 2.7%; Cl, 48.2%). Elution with benzene gave a solid as colourless needles which were recrystallised from petroleum ether, m.p. = 120-122°C, and this solid was 1,2,4a,8b-tetrachloro-1,2,4a,8b-tetrahydro-6-hydroxybiphenylene (Found: C, 52.2%; H, 3.3%; Cl, 38.5%. $C_{12}H_9Cl_3O$ requires C, 52.3%; H, 3.3%; Cl, 38.6%).

Dechlorination of 1,2,4a,8b-tetrachloro-1,2,4a,8b-tetrahydrobiphenylene

The tetrachloride (0.21g), zinc dust (0.56g) and acetic acid (20 ml) were refluxed for 8 hours, then poured into water (100 ml). The organic products were collected by extraction with ether, the solvent removed by reduced pressure to give an oil (0.22g) and this was treated with 2,4,7-trinitrofluorenone in benzene-methanol to give biphenylene-2,4,7-trinitrofluorenone complex (0.08g) as deep red needles after recrystallisation from ethanol, the m.p. and mixed m.p. = 156-157°C.

Under similar conditions the trichlorohydroxy compound gave biphenylene which was also isolated as the 2,4,7-trinitrofluorenone complex.

2. Chlorination of biphenylene with sulphuryl chloride

Sulphuryl chloride was purified by fractional distillation. The impurity, which was yellow (free chlorine) was first removed, the distillation was then stopped and the system was flushed with carbon dioxide before continuing the distillation. In this way a colourless product (b.p. 68.8°/750 mm.) could be obtained.

Chloroform was purified by shaking it three times with small volumes (5%) of concentrated sulphuric acid, then thoroughly washed with water, several times, drying it over anhydrous calcium chloride and distilling. Pure chloroform has a b.p. 61°/670 mm.

(i) At room temperature

Biphenylene (3.04g, 0.02 mole) was dissolved in chloroform (20 ml.) while sulphuryl chloride (2.5 ml., 0.03 mole) was added. The reaction mixture was left standing in the dark at room temperature for a week. The mixture was then poured into water (200 ml.) to destroy the excess of sulphuryl chloride. The organic layer was collected, while the aqueous layer was extracted with ether and dried over anhydrous magnesium sulphate. The solvents were removed under reduced pressure to give an oil (3.92g), which was adsorbed on a silica column (30 x 2.5 cm.). Elution with petroleum ether (40 - 60°) gave the following products:-

a) pale yellow solid (0.62g, 20% yield) of 2-chloro-biphenylene, m.p. = 66-67°C, from aqueous methanol, which was identical with that prepared before.

b) pale yellow solid of unreacted biphenylene.

c) colourless solid from petroleum ether (40 - 60°), m.p. = 101-102°C , 1,2,4a,8b-tetrachloro-1,2,4a,8b-tetra-hydrobiphenylene (0.01g, .2% yield) identical with that prepared before.

d) pale yellow oil, which was very difficult to obtain as crystals.

(ii) At reflux temperature

A. With solvent

As above experiment but the reaction mixture was heated under gentle reflux (60-70°C) for six hours, then left to stand at room temperature overnight.

The organic layer was collected, dried over calcium chloride, then the solvent was removed under reduced pressure to give the following:-

a) pale yellow solid from aqueous methanol, m.p. = 66-67°C, 2-chlorobiphenylene (0.31g, 10% yield).

b) pale yellow solid from methanol, m.p. = 110-111°C, of unreacted biphenylene.

B. Without solvent

Biphenylene (3.04g, 0.02 mole) and sulphuryl chloride (6.5 ml., 0.077 mole) were heated together under gentle reflux for six hours. Then the reaction mixture was left to stand at room temperature overnight, then poured into water (500 ml.), extracted with ether, followed by evaporation of the solvent to give an oil (4.25g) and chromatography, as before, gave the following products:-

a) pale yellow solid of 2-chlorobiphenylene (0.35g, 15% yield)

b) pale yellow solid of unreacted biphenylene

c) pale yellow oil which was difficult to solidify.

3. Chlorination of biphenylene with phosphorus pentachloride

Methylene chloride was purified by washing with 5% sodium carbonate solution, followed by water, several times, and dried over anhydrous calcium chloride, and then fractionally distilled. The fraction, b.p. 40-41°C, was collected.

A stirred solution of biphenylene (0.78g) and phosphorus pentachloride (3.0g, 2.8 equivalent) in dry methylene chloride (40 ml.) were boiled under reflux for four hours and then allowed to cool. The brown coloured solution was changed to pale yellow after the addition of water. The product was collected by extraction with ether, dried over magnesium sulphate, then the solvent was removed under reduced pressure to give a solid (0.81g), m.p. = 82-95°C.

This was purified by column chromatography on silica gel. Elution with n-hexane gave pure unreacted biphenylene (0.71g), m.p. = 110-111°C (identified by U.V. and I.R. spectra).

4. Chlorination of biphenylene with molecular chlorine in chloroform at 50°C

Biphenylene (1.52g, 0.01 mole) was dissolved in chloroform (20 ml.); chlorine (1.42g, 0.02 mole) in chloroform (20 ml.) was added dropwise (while the temperature was kept at 50°C) during 15 minutes. The reaction mixture was refluxed at the same temperature for three hours, then cooled and poured into water (100 ml.). The solvent was evaporated under reduced pressure to give a solid (1.67g). This solid was absorbed as before, giving the following:-

a) 2-chlorobiphenylene, identical with that prepared before, in 5% yield

b) unreacted biphenylene, identified by U.V. and I.R. spectra.

Preparation of 2-methoxybiphenylene

2-Methoxybiphenylene was prepared from 2-acetyl-[1],[2] or 2-benzoylbiphenylene[3],[4], which were both converted into 2-acetoxy- or 2-benzoyloxybiphenylene by oxidation with peracetic acid. 2-Acetoxybiphenylene, on hydrolysis and methylation with dimethyl sulphate, gave 2-methoxybiphenylene which was recrystallised from petroleum ether (40 - 60°C) to give a pure sample of 2-methoxybiphenylene as long, thick, lemon needles, m.p. = 69-70°C.

Also 2-methoxybiphenylene was prepared from 2-benzoyloxybiphenylene on methylation with dimethyl sulphate in the presence of sodium hydroxide.

Alternate portions of dimethyl sulphate (15 ml) and sodium hydroxide (10.5g) in water (18 ml) were added to 2-benzoyloxybiphenylene (1.3g) in methanol (20 ml) during a period of twenty minutes so that the temperature of the reaction was kept at ca. 60°C. After all the portions were added the mixture was then poured into water (200 ml) and the precipitate was collected (1.25g) and purified by steam distillation to give pure 2-methoxybiphenylene (0.96g) which was recrystallised from petroleum ether to give long, thick, lemon needles, m.p. and mixed m.p. = 68-70°C (lit.[1],[2], 68-69, 69-70°C).

1. Chlorination of 2-methoxybiphenylene with molecular chlorine in acetic acid at 25°C

2-Methoxybiphenylene (0.91g) was dissolved in acetic acid (10 ml) and chlorine (0.41g) in acetic acid (10 ml) was added gradually to the biphenylene solution. The reaction mixture was left to stand at room temperature for

two hours, and then poured into water (200 ml) and the product was collected in ether and dried over magnesium sulphate.

Concentration of the mixture to remove the solvent under reduced pressure gave an oil (1.25g). The oil product was purified by column chromatography on silica gel (24 x 2 cm) on n-hexane.

The yellow portion was collected and the solid was recrystallised three times from methanol to give a pure compound of 2-methoxy-3-chlorobiphenylene, m.p. = 130-132 as bright yellow plates (0.051g) in 4.6% yield.

Found C, 71.9%; H, 4.1%; Cl, 16.2% $C_{13}H_9ClO$

Require C, 72.1%; H, 4.2%; Cl, 16.4%

2. Chlorination of 2-methoxybiphenylene with sulphuryl chloride

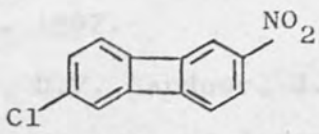
2-Methoxybiphenylene (0.46g, 0.04 mole) was dissolved in chloroform or nitrobenzene (15 ml.) and the sulphuryl chloride (0.5 ml.) was added. The reaction mixture was left to stand at room temperature for ten days, or heated under gentle reflux for six hours; then it was poured into water (200 ml.). The product was collected by extraction with ether, dried over magnesium sulphate; the solvent was removed under reduced pressure to give a green/yellow oil (0.53g).

Chromatography, as before, gave a starting material of 2-methoxybiphenylene, which was identical with that prepared before.

Preparation of 2-nitrobiphenylene

2-Nitrobiphenylene was prepared by the nitration of biphenylene with concentrated nitric acid in acetic acid/ acetic anhydride at 0°C and was purified by steam distillation to give pure 2-nitrobiphenylene as deep yellow needles, m.p. = 106-107°C from petroleum ether (40-60°C).

Chlorination of 2-nitrobiphenylene



2-Nitrobiphenylene (1.0g) was dissolved in acetic acid (40 ml.). Chlorine (1.42g, 0.02 mole) in acetic acid (10 ml.) was added dropwise during a fifteen minute period to the biphenylene solution. The reaction mixture was kept standing at room temperature overnight, then it was poured into water (400 ml.). The solid was collected by filtration.

2-Nitrobiphenylene was removed by steam distillation and the residue was extracted with ether and dried over magnesium sulphate. The solvent was removed under reduced pressure to give a yellow oil (0.22g) which was adsorbed on a silica column (24 x 2.5 cm.). Elution with a mixture of cyclohexane and benzene (3 : 1) gave 2-nitro-6-chloro-biphenylene, which was crystallised from methanol as bright yellow needles, m.p. = 189-190°C.

Found C, 61.98%; H, 2.50%; Cl, 15.10% $C_{12}H_6ClNO_2$

Require C, 62.20%; H, 2.60%; Cl, 15.30%

3.10 References

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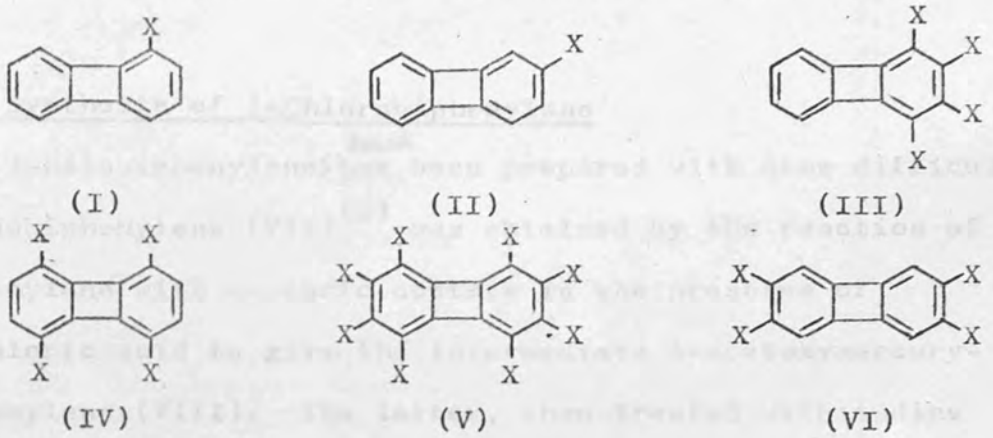
CHAPTER FOUR*

SYNTHESIS OF MONO- AND DI-CHLOROBIPHENYLENE

* References for this chapter will be found on page 120.

SYNTHESIS OF MONO- AND DI-CHLOROBIPHENYLENES



(I) (II) (III)

(IV) (V) (VI)

4.1 Introduction

Direct substitution of halogens in biphenylene is complicated, and made very difficult[1], especially at position 1, by the tendency of the hydrocarbon to undergo addition reactions as well as substitution[2],[3] (see Chapters 2 and 3).

1-Halobiphenylene (I) is very difficult to obtain by direct halogenation, but 2-halobiphenylene (II) can be prepared more easily, by the action of halogen on biphenylene[1],[2],[3],[4],[6].

Recently, 2-bromo- and 2-chlorobiphenylene (II, X = Br or Cl) were prepared by bromination of biphenylene in carbon tetrachloride in the presence of thallium (III) acetate[4], and by thermal decomposition of 2-aminobiphenylene-3-carboxylic acid[5] after diazotisation, in the presence of 1,2-dichloroethane, in 88% and 9% yields respectively.

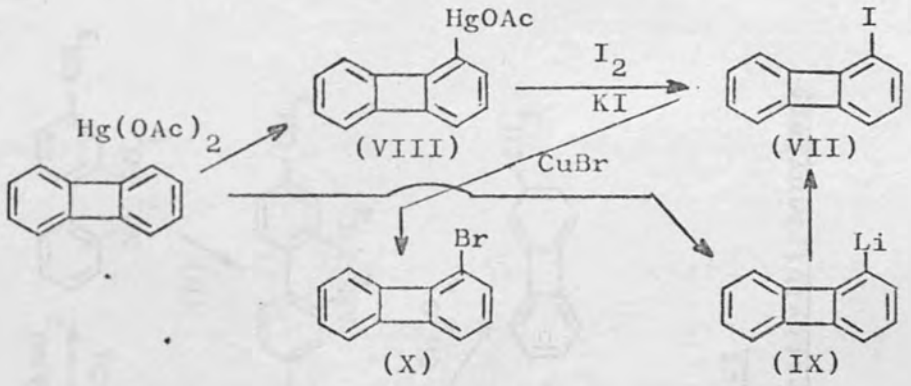
Poly-halobiphenylenes[7],[8],[9] have been obtained by the pyrolysis of the corresponding phthalic anhydride[8] and by vacuum pyrolysis of octachloro- derivatives of benzo(c)cinnoline at high temperature[7], or by chlorination

and bromination of biphenylene after sulphonation, with potassium chlorate or molecular bromine, respectively.

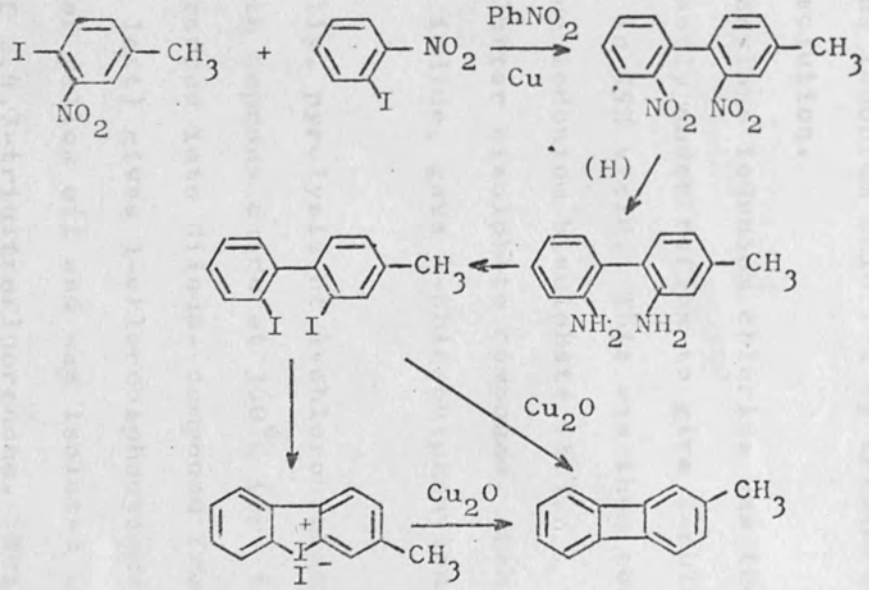
4.2 Synthesis of 1-Chlorobiphenylene

1-Halobiphenylenes ~~has~~ have been prepared with some difficulty; 1-iodobiphenylene (VII)[2] was obtained by the reaction of biphenylene with mercuric acetate in the presence of perchloric acid to give the intermediate 1-acetoxymercury-biphenylene (VIII). The latter, when treated with iodine in potassium iodide, gave 1-iodobiphenylene (VII). Also, 1-iodobiphenylene was obtained in poor yield by the reaction of iodine with 1-lithiobiphenylene[10] (IX).

1-Bromobiphenylene (X) was prepared by the reaction of 1-iodobiphenylene with cuprous bromide in N,N-dimethyl-formamide in 59% yield.

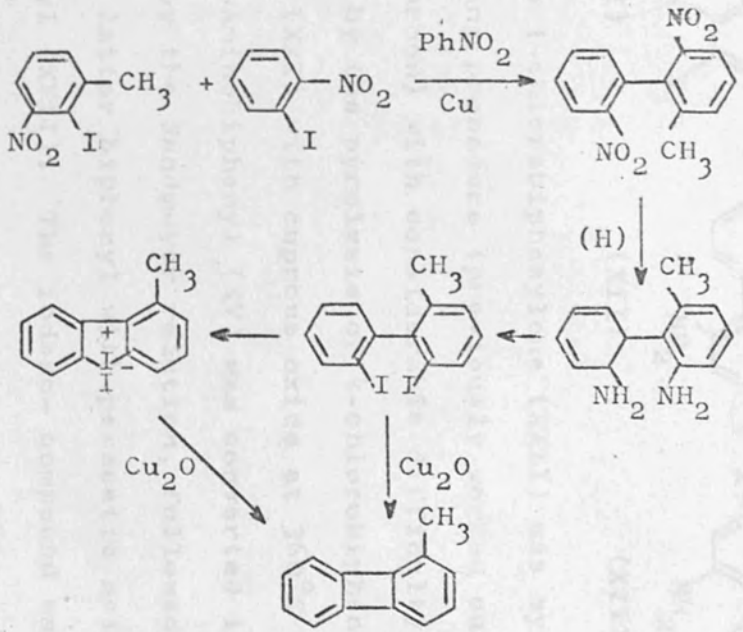


A 1-substituted biphenylene ultimately results from 2-aminobiphenyl substituted at positions 3 or 6 (XI) or (XII) (see scheme 4.2 for 1-methylbiphenylene), while 2-substituted biphenylene result from either 4 or 5 substituted 2-amino-biphenyls (XIII) or (XIV) (see scheme 4.1 for 2-methyl-biphenylene).



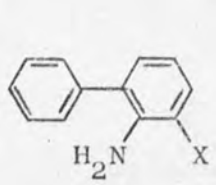
Scheme 4.1

Synthetic routes of 2-methylbiphenylene

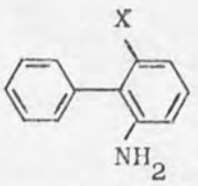


Scheme 4.2

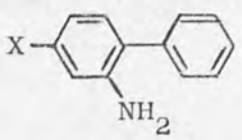
Synthetic routes of 1-methylbiphenylene



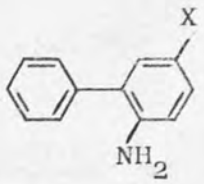
(XI)



(XII)



(XIII)



(XIV)

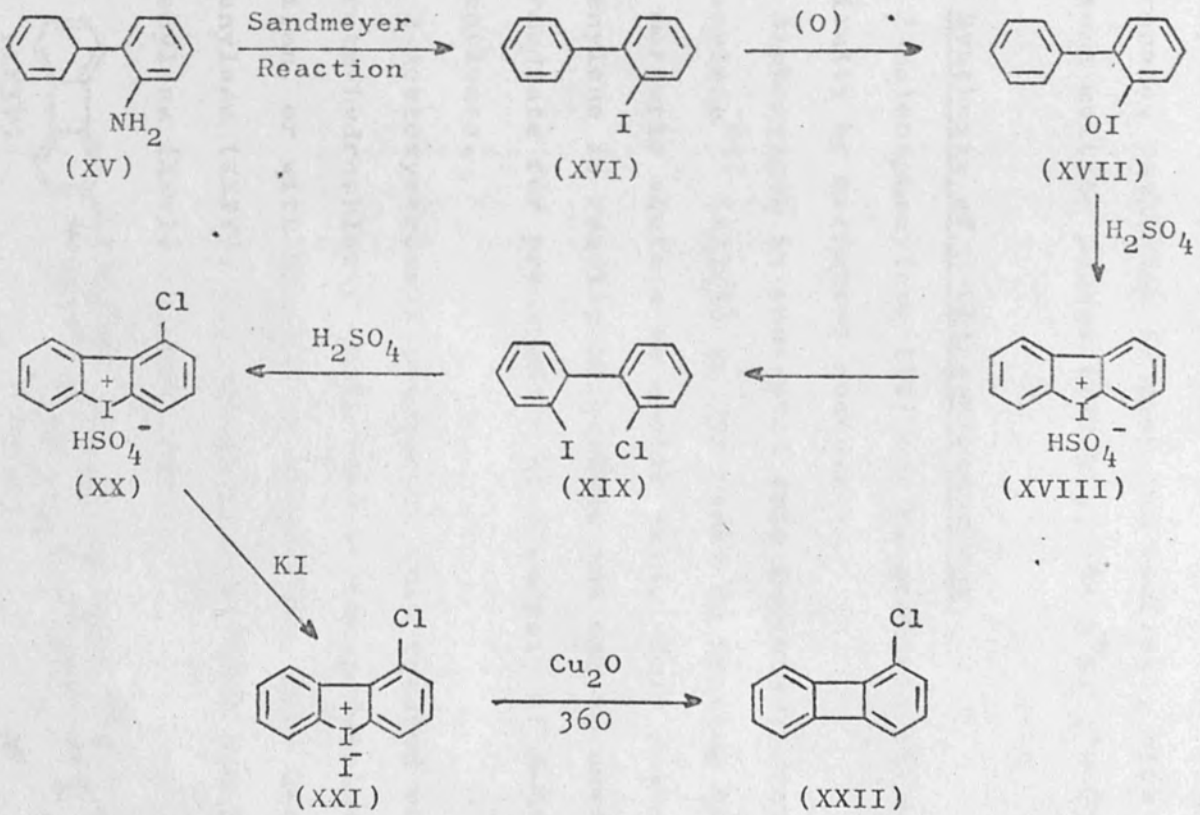
So 1-chlorobiphenylene (XXII) was synthesised by the following procedure (previously worked out for the parent hydrocarbon) with considerable difficulty and in poor yield, by the pyrolysis of 4-chlorobiphenylene iodonium iodide (XXI) with cuprous oxide at 360°C (scheme 4.3).

2-Aminobiphenyl (XV) was converted into 2-iodobiphenyl (XVI) by the Sandmeyer reaction, followed by oxidation of the latter biphenyl with peracetic acid to obtain 2-iodoso-biphenyl (XVII). The iodoso- compound was cyclised by sulphuric acid and acetic anhydride to give biphenylene iodonium bisulphate (XVIII), which was then converted into biphenylene iodonium chloride by treatment with hot sodium chloride solution.

Biphenylene iodonium chloride was then decomposed by heating gently under reflux to give 2-chloro-2'-iodobiphenyl (XIX)[11] in 55% yield. This was then converted to 4-chloro-biphenylene iodonium bisulphate (XX).

The latter bisulphate compound, when treated with potassium iodide, gave 4-chlorobiphenylene iodonium iodide (XXI).

Finally, pyrolysis of 4-chlorobiphenylene iodonium iodide with cuprous oxide at 360°C (the iodonium iodide is first converted into diiodo- compound from which the iodine atoms are lost) gives 1-chlorobiphenylene (XXII) in a large quantity of yellow oil and was isolated by means of its complex of 2,4,7-trinitrofluorenone. This was decomposed



Scheme 4.3

Synthetic routes of 1-chlorobiphenylene

by passing over an alumina column to give 1-chlorobiphenylene (XXII) as an oil in 5% yield.

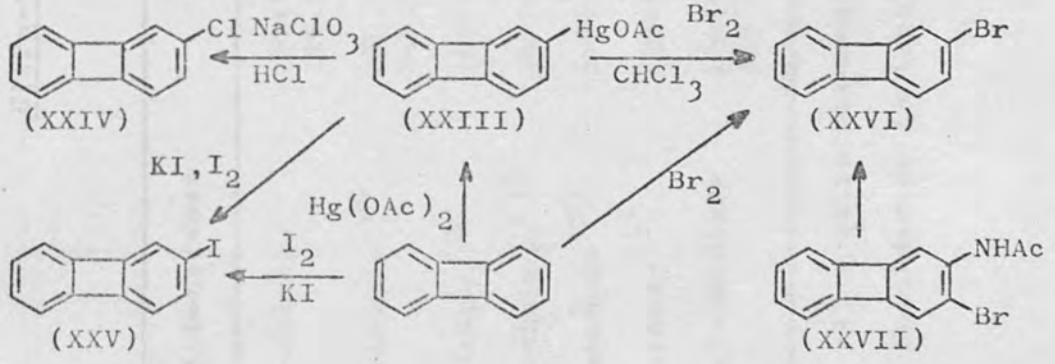
The ultra-violet absorption of 1-chlorobiphenylene is at nearly the same wavelength as both 1-iodo- and 1-bromo-biphenylenes (Table 4.1) and also form with 2,4,7-trinitro-fluorenone, complexes as deep red leaflets, with nearly the same melting points (177-9°C; 181-3°C; 179-80°C).

4.3 Synthesis of 2-Chlorobiphenylene

2-Halobiphenylene (II) can be prepared without difficulty by different routes:-

Biphenylene is converted into 2-acetoxymercury-biphenylene[1] (XXIII) in 79% yield by heating biphenylene with mercuric acetate in acetic acid. This 2-acetoxymercury-biphenylene is readily accessible and can be used as an intermediate for preparation of a variety of 2-halo-biphenylenes.

2-Acetoxymercurybiphenylene, when treated with sodium chlorate-hydrochloric acid, with iodine-potassium iodide solution, or with bromine in chloroform, gave 2-chloro-biphenylene (XXIV), 2-iodobiphenylene (XXV) and 2-bromo-biphenylene (XXVI) respectively.



2-Chlorobiphenylene (XXIV) was prepared from 2-acetamido-

Table 4.1

Ultra-violet Absorption Characteristics of Halobiphenylenes*

Biphenylenes	Absorption maxima (mu) and extinction coefficient (log ε)
1-chloro-	247(4.33); 256(4.51); 329•(3.69); 340(3.45); 343(3.48); 352(3.29); 359.5(3.61).
1-bromo-(2)	246.5(4.47); 255(4.67); 306.5(3.77); 327.5(3.13); 352(3.11); 341(3.41) 345.5(3.41); 360(3.60).
1-iodo-(2)	249(4.50); 258.5(4.66); 330.5(3.81); 334.5(3.30); 347.5(3.59); 363(3.74).
2-chloro-(1)	244(4.49); 252(4.72); 344(3.54); 363(3.66).
2-bromo-(1)	245(4.59); 253(4.79); 344(3.61); 363(3.76).
2-iodo-(1)	257(4.82); 345(3.79); 364(3.95).
1,3-dichloro	206(4.60); 248(4.95); 257.5(5.18); 286.5(3.36); 301•(3.19); 313.5(3.33); 335•(3.61); 330(3.61); 344(3.87); 348(3.85); 364(3.99).

* All spectra determined in 95% ethanol

• Shoulder or inflection

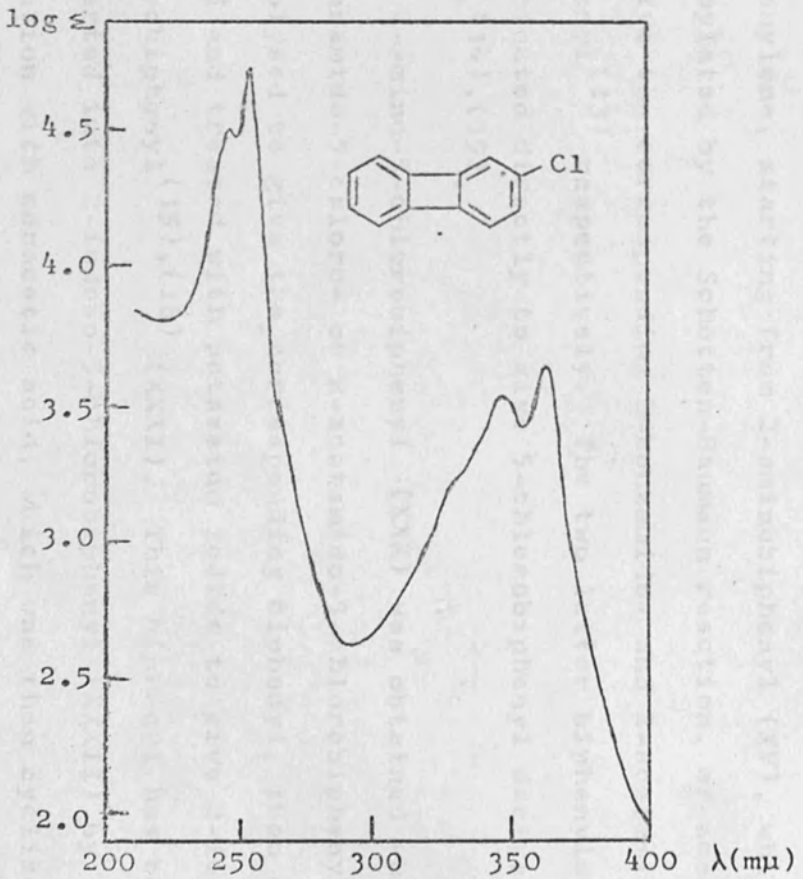


Fig. 4.1

Ultra-violet Absorption of

2-chlorobiphenylene in 95% ethanol

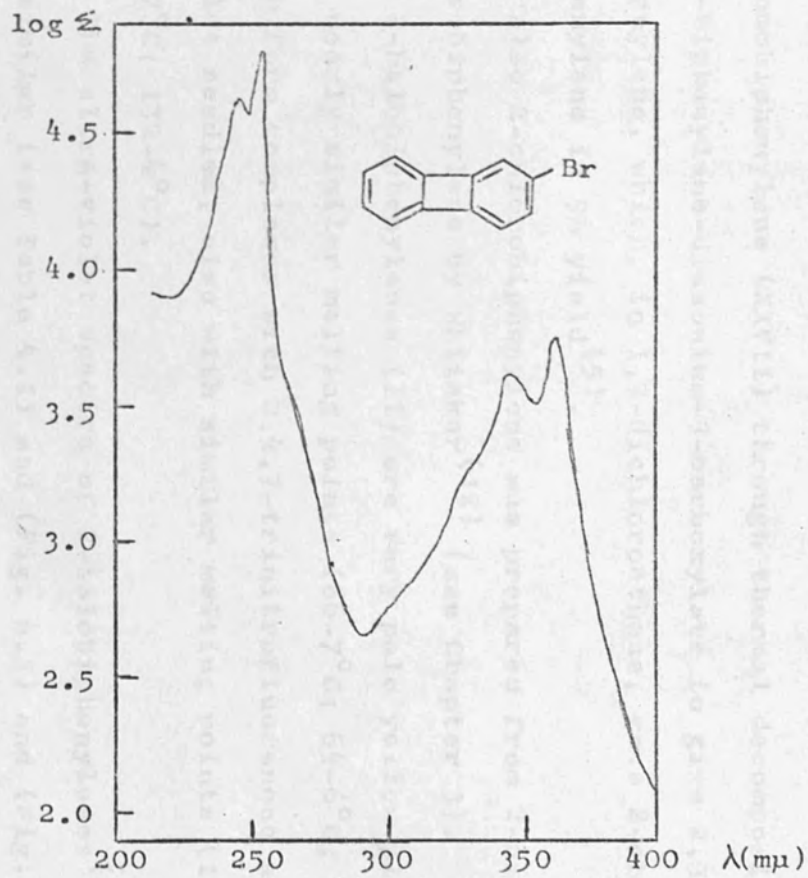


Fig. 4.2

Ultra-violet Absorption of

2-bromobiphenylene in 95% ethanol

3-bromobiphenylene (XXVII) through thermal decomposition of 2-biphenylene-diazonium-3-carboxylate to give 2,3-dihydrobiphenylene, which, in 1,2-dichloroethane, gave 2-chlorobiphenylene in 9% yield[5].

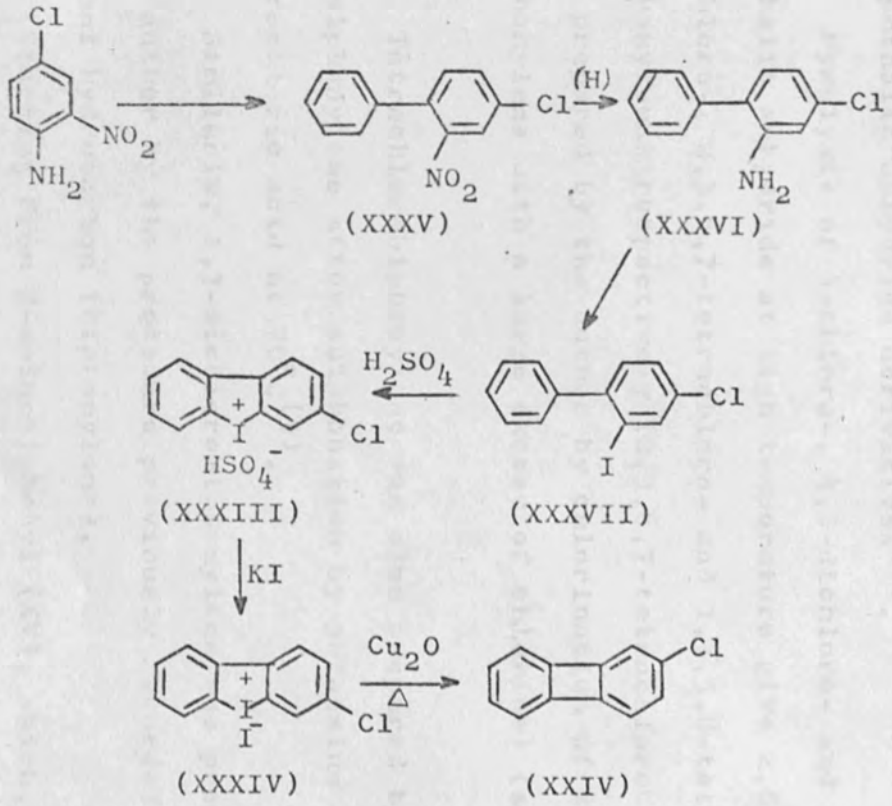
Also 2-chlorobiphenylene was prepared from 2-nitro-6-chlorobiphenylene by Whitaker[12] (see Chapter 3).

2-Halobiphenylenes (II) are very pale yellow plates with nearly similar melting points (66-7°C; 64-6°C; 63-4°C) which form complexes with 2,4,7-trinitrofluorenone as scarlet needles, also with similar melting points (133-4°C; 135-7°C; 132-4°C).

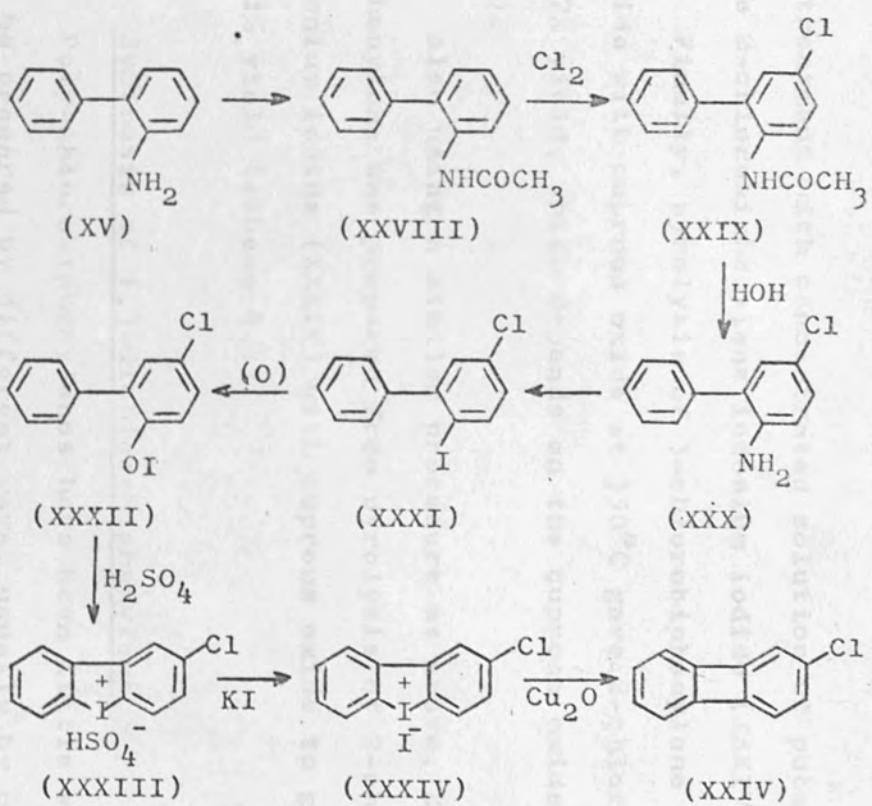
The ultra-violet spectra of 2-halobiphenylenes[1] are similar (see Table 4.1) and (Fig. 4.1) and (Fig. 4.2).

2-Chlorobiphenylene was prepared by the author by two routes; by the synthesis used for the parent hydrocarbon biphenylene, starting from 2-aminobiphenyl (XV), which was benzoylated by the Schotten-Baumann reaction, or acetylated[13] to give the corresponding 2-benzamido- and 2-acetamido-biphenyl[13] respectively. The two latter biphenyls chlorinated directly to give 5-chlorobiphenyl derivatives[14],[15].

2-Amino-5-chlorobiphenyl (XXX) was obtained when 2-benzamido-5-chloro- or 2-acetamido-5-chlorobiphenyls were hydrolysed to give the corresponding biphenyl, then diazotised and treated with potassium iodide to give 2-iodo-5-chlorobiphenyl[15],[16] (XXXI). This biphenyl has been converted into 2-iodoso-5-chlorobiphenyl (XXXII) by oxidation with peracetic acid, which was then cyclised with concentrated sulphuric acid to give, in high yield, 3-chlorobiphenylene iodonium bisulphate[17] (XXXIII), which



Scheme 4.4



Scheme 4.5

Synthetic routes of 2-chlorobiphenylene

on treatment with concentrated solution of potassium iodide gave 2-chlorobiphenylene iodonium iodide (XXXIV).

Finally, pyrolysis of 3-chlorobiphenylene iodonium iodide with cuprous oxide at 350°C gave 2-chlorobiphenylene in 7% yield, which depends on the cuprous oxide used (scheme 4.5).

Also using a similar procedure as above, 2-chlorobiphenylene was prepared from pyrolysis of 2-chlorobiphenylene iodonium iodide (XXXIV) with cuprous oxide to give biphenylene in 1% yield (scheme 4.4).

4.4 Synthesis of 1,3-dichlorobiphenylene

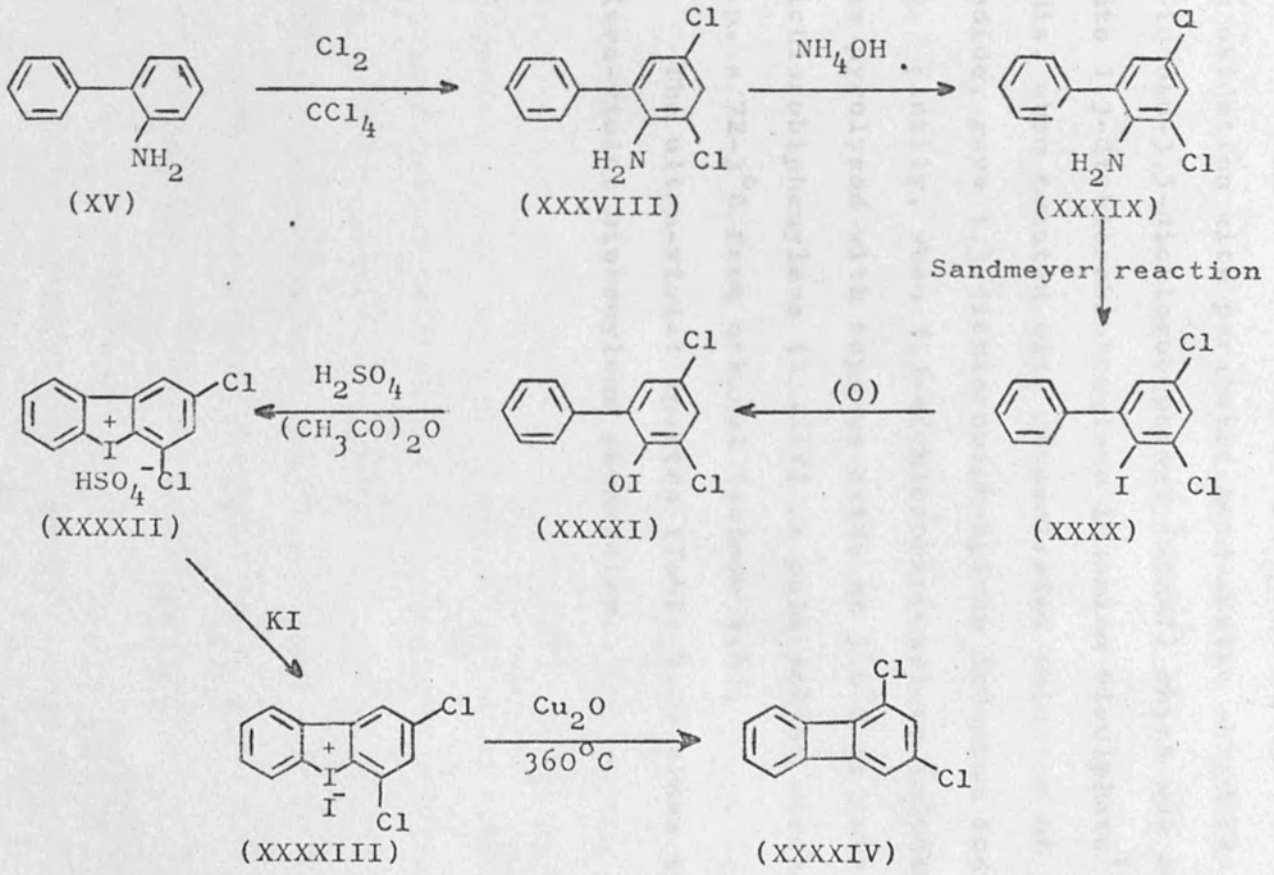
Poly-chlorobiphenylenes have been little studied, and can be prepared by different ways, usually by pyrolysis of phthalic anhydride derivatives[8].

Pyrolysis of 4-chloro-, 4,5-dichloro- and 3,6-dichlorophthalic anhydride at high temperature give 2,6 (2,7)-dichloro-, 2,3,6,7-tetrachloro- and 1,4,5,8-tetrachlorobiphenylenes respectively (2,3,6,7-tetrachlorobiphenylene was prepared by the author by chlorination of 2-chlorobiphenylene with a large excess of chlorine) (see Chapter 5).

Tetrachlorobiphenylene was also prepared by chlorination of biphenylene after sulphonation by potassium chlorate in hydrochloric acid at 70°C[9].

Similarly, 1,3-dichlorobiphenylene was prepared by the author by the procedure previously recorded for the parent hydrocarbon (biphenylene).

Starting from 2-aminobiphenyl (XV), which, with excess chlorine at freezing temperature, in carbon tetrachloride,



Scheme 4.6

Synthetic routes of 1,3-dichlorobiphenylene

to give 3,5-dichloro-2-aminobiphenyl[18] hydrochloride (XXXVIII) which when warmed with ammonia gave 3,5-dichloro-2-aminobiphenyl[18] (XXXIX). This converted into 2-iodo-3,5-dichlorobiphenyl[17] (XXXX) by the Sandmeyer method, which on oxidation with peracetic acid-acetic anhydride gives 2-iodoso-3,5-dichlorobiphenyl (XXXXI) which was converted into 1,3-dichlorobiphenylene iodonium bisulphate[17] (XXXXII). This, when treated with concentrated solution of potassium iodide, gave 1,3-dichlorobiphenylene iodonium iodide (XXXXIII).

Finally, when 1,3-dichlorobiphenylene iodonium iodide was pyrolysed with cuprous oxide at 360°C it gave 1,3-dichlorobiphenylene (XXXXIV) as pale yellow needles, m.p. = 72-3°C from ethanol (scheme 4.6).

The ultra-violet spectra (Table 4.1) shows typical ultra-violet biphenylene absorption.

4.5 Experimental Section

1. Preparation of 1-Chlorobiphenylene

1-Chlorobiphenylene was synthesised from 2-chloro-2'-iodobiphenyl through the chlorobiphenylene iodonium bisulphate (see page 85 and 86).

a) Biphenylene iodonium chloride and 2-chloro-2'-iodobiphenyl

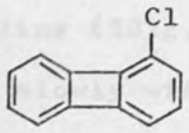
Biphenylene iodonium bisulphate (55g) was dissolved in boiling water (2 litres) and then heated with a hot solution of saturated sodium chloride (56g) in 400 ml. of water. The hot filtered solution was cooled, and the precipitate of biphenylene iodonium chloride was filtered off and washed with a small amount of water, then dried. The dry biphenylene iodonium chloride was heated gently under reflux with an air condenser at approximately 195°C (a metal bath is preferable). The salt decomposed, giving iodine vapour and a liquid. When no more salt decomposed on further heating the cooled reaction mixture was treated with ether and the ether solution was washed with sodium metabisulphite solution to remove iodine before drying with sodium sulphate. Evaporating the solvent under reduced pressure gave a solid which was recrystallised from ethanol; this solid was 2-chloro-2'-iodobiphenyl (25g, 55%), m.p. = 62-4°C (lit[11] 62-4°C).

b) 4-Chlorobiphenylene iodonium iodide

2-Chloro-2'-iodobiphenyl (25g) was dissolved in acetic acid (100 ml.) and added to 36% peracetic acid (50 ml.) and sulphuric acid (50 ml.) was added slowly keeping the temp-

erature below 30°C all the time. The mixture was then stirred for three hours. Two litres of water and potassium iodide (25g) were then added to the mixture.

The mixture was then boiled and on cooling a yellow precipitate was obtained, which was filtered off, washed with methanol and dried. This solid was 4-chlorobiphenylene iodonium iodide (20g, 97%), m.p. = 184-90°C (decomposed at 190°C) and recovered 2-chloro-2'-iodobiphenyl (10g).



c) 1-Chlorobiphenylene

4-Chlorobiphenylene iodonium iodide was pyrolysed with cuprous oxide at 350°C to give large quantities of a yellow oil, which was boiled with 2,4,7-trinitrofluorenone in 10% ethyl acetate-90% ethanol (75 ml.). On cooling this gave a red crystalline precipitate, which was crystallised from ethanol to give red leaflet crystals, m.p. = 179-80°C. By chromatography on alumina 1-chlorobiphenylene was liberated from the complex as a yellow/green oil (0.4g, 5%)

Found C, 59.9%; H, 2.4%; N, 8.2%; $C_{25}H_{12}N_3O_7$

Requires C, 59.8%; H, 2.3%; N, 8.4%.

2. Preparation of 2-Chlorobiphenylene

I From 2-amino-4-chlorobiphenyl (XXXVI)

2-Chlorobiphenylene was prepared from 4-chloro-2-iodobiphenyl through the appropriate chlorobiphenylene iodonium bisulphate and iodide.

a) 4-Chloro-2-nitrobiphenyl

4-Chloro-2-nitroaniline (121g, 0.7 mole) in benzene (1.5 litres) was treated slowly with pentyl nitrite (115 ml., 0.85 mole) and the resulting mixture was boiled under reflux until the evolution of nitrogen and other gases ceased. The red benzene solution was washed with sodium hydroxide to remove phenols, and with hydrochloric acid (6M) to remove bases. After further washing with water, the dried (Na_2SO_4) solution was concentrated under reduced pressure, and distilled. m-Chloronitrobenzene (6g, 5%) was isolated as a fore-run (b.p. 88-95°/5 mm.) to the biaryl fraction, b.p. 174-8°/5 mm. On recrystallisation of the solid distillate from ethanol, 4-chloro-2-nitrobiphenyl (50g, 31%) was obtained, m.p. = 28.0-28.6°C.

b) 4-Chloro-2-iodobiphenyl

4-Chloro-2-nitrobiphenyl (50g, 0.21 mole) was reduced with iron dust (50g) with aqueous acetic acid. Each addition of the nitro-compound caused an exothermic reaction, and the mixture was boiled for two hours after the addition to complete the reduction. Benzene extraction of the reaction mixture, followed by treatment with hydrochloric acid (2M) gave a precipitate of the amine hydrochloride

which, on filtration, washing with ethanol, and treatment with ammonia, gave the free base (34g, 70%). This was diazotised in hydrochloric acid (6M) and the diazonium solution was treated with potassium iodide (120g, excess) to give, after standard work-up, 4-chloro-2-iodobiphenyl, b.p. 148°/4 mm. (36g, 80%).

c) 2-Chlorobiphenylene iodonium iodide

4-Chloro-2-iodobiphenyl (36g) was added to a solution of hydrogen peroxide (30%, 50 ml.) in sulphuric acid (0.5 ml.) - acetic anhydride (200 ml.) mixture after the exothermic reaction, which was held at below 25°C, had finished. A further quantity of acetic anhydride (80 ml.) was added, and the reaction allowed to proceed overnight. Sulphuric acid (40 ml.) was then added slowly, and after seven hours the thick precipitation of chlorobiphenylene iodonium salts was filtered, and was washed with water, ethanol and ether to give 39g product (83% calculated as bisulphate), m.p. = 300°C. This was stirred with a dimethylformamide solution of potassium iodide (20g) at ca. 100°C for five hours, and poured into water to give the corresponding chlorobiphenylene iodonium iodide (37g, 89%), m.p. = 205-215°C (d).

d) 2-Chlorobiphenylene

Four batches of 2-chlorobiphenylene iodonium iodide (9g) were pyrolysed successfully with cuprous oxide (80g) at 350°C for thirty minutes. The waxy sublimate from these reactions was combined, and treated in acetone-ethanol mixture with 2,4,7-trinitrofluorenone. The resulting

scarlet complex, m.p. = 123-5°C, was recrystallised and was then decomposed by chromatography upon alumina to give 2-chlorobiphenylene (30mg, m.p. = 66-67°C).

II From 2-amino-5-chlorobiphenyl (XXX)

2-Amino-5-chlorobiphenyl was prepared by acetylation of 2-aminobiphenyl to give 2-acetamidobiphenyl[13], which was chlorinated directly to give 2-acetamido-5-chlorobiphenyl by the method of Bell and Gibson[14].

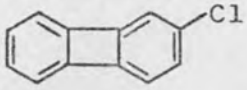
a) Preparation of 2-iodo-5-chlorobiphenyl[16]

A solution of 2-acetamido-5-chlorobiphenyl (13.8g, ~0.057 mole) in absolute ethanol (200 ml.) and concentrated hydrochloric acid (18 ml.) was heated under reflux for three hours. The solvent was removed by distillation to give the crude hydrochloride salt. To this salt was added water (25 ml.) and concentrated hydrochloric acid (25 ml.).

The suspension was cooled with stirring to -5°C, and crushed ice (55g) was added. The amino salt was then diazotised with a solution of sodium nitrite (6g) in water (25 ml.). After the diazonium suspension had been stirred at 5°C for 15 minutes, a solution of potassium iodide (30g) in water (50 ml.) was added over a period of 1½ hours. This mixture was stirred at 10°C for 2 hours and then heated with shaking on a steam bath until the gas evolution had ceased and the temperature of the mixture had reached 80°C. The product was extracted into benzene and removal of the solvent gave crude 2-iodo-5-chlorobiphenyl (10g, ~62% yield) as a black oil, which was distilled under reduced pressure (b.p. 125-150°/0.6 mm.).

b) 3-Chlorobiphenylene iodonium iodide

2-Iodo-5-chlorobiphenyl (7g) in acetic acid (25 ml.) was added dropwise at 0°C to a 40% solution of peracetic acid (30 ml.). The mixture was kept at room temperature for 16 hours. This solution, which then contained the iodoso-compound, was treated at 0°C with concentrated (18M) sulphuric acid (7 ml.) and the mixture was left at room temperature for 5 hours, then water (120 ml.) was added and the whole mixture was stirred for one hour and then extracted with benzene. The aqueous layer was treated with aqueous sodium hydrogen sulphite until no iodine was liberated on addition of potassium iodide, and a concentrated solution of potassium iodide was then added until no further precipitation of the iodonium iodide occured. This product was collected and washed well with water in which it is almost insoluble, and then dried (yield about 6g, m.p. = 210-220°C) (decomposed).



c) 2-Chlorobiphenylene

3-Chlorobiphenylene iodonium iodide (4g) was heated at 360°C for 20 minutes in the usual way with cuprous oxide (60g). The distillate was collected in methanol, and was converted into the 2,4,7-trinitrofluorenone complex as scarlet needles, m.p. = 132-134°C (lit.[1] 133-134°C), which were decomposed by passing over alumina in benzene to give pure 2-chlorobiphenylene as very pale yellow plates, m.p. = 66-67°C from aqueous ethanol (7% yield).

3. Preparation of 1,3-Dichlorobiphenylene

Chlorination of 2-aminobiphenyl and preparation of 2-iodo-1,3-dichlorobiphenyl

2-Aminobiphenyl (68g, 0.40 mole) was dissolved in carbon tetrachloride (1 litre) and a solution of chlorine (60.4g, 0.85 mole) in carbon tetrachloride (40 ml.) was added at 5-10°C (ice-salt cooling). The white precipitate which separated was collected after one hour, washed several times with carbon tetrachloride and dried in air. This precipitate of 2-amino-3,5-dichlorobiphenyl hydrochloride was dissolved in water (1 litre) and concentrated sulphuric acid (25 ml.) and to this solution was added slowly a solution of sodium nitrite (27g) in water (50 ml.) while keeping the temperature at 0-5°C. The reaction mixture was poured into a solution of potassium iodide (150g) in water (250 ml.), keeping the temperature below 5°C.

The mixture was kept overnight, then warmed at 60°C. Free iodine was removed by addition of sodium thiosulphate and the product was collected by extraction with ether. The organic layer was washed with sodium bicarbonate solution and dried over sodium sulphate. The ether was removed under reduced pressure giving a black oil which was purified by vacuum distillation, collecting the fraction, b.p. 171-178°/4 mm. as 2-iodo-3,5-dichlorobiphenyl (36g, 25%).

1,3-Dichlorobiphenylene iodonium bisulphate

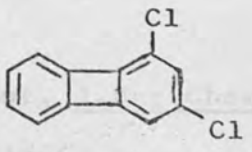
2-Iodo-3,5-dichlorobiphenyl (35g) was dissolved in acetic anhydride (50 ml.) and the solution was added dropwise to peracetic acid (40%, 70 ml.). The initially cloudy solution then gave a clear dark solution which subsequently lightened and became opaque. The mixture was stirred at room temperature for 20 hours then cooled to 5°C and sulphuric acid (40 ml.) was added dropwise with the temperature maintained at 5-10°C. The mixture was kept at room temperature for 4 hours, then cold water (500 ml.) was added, and the whole was stirred for a further one hour.

The precipitate was filtered off by suction giving 1,3-dichlorobiphenylene iodonium bisulphate (41g), m.p. = 245-250°C.

1,3-Dichlorobiphenylene iodonium iodide

1,3-Dichlorobiphenylene iodonium bisulphate (41g) was converted quantitatively to the iodide by dissolving in dimethylformamide and treatment with an excess of potassium iodide solution.

1,3-Dichlorobiphenylene



A mixture of 1,3-dichlorobiphenylene iodonium iodide (3g) and cuprous oxide (25g) was heated as in the previous biphenylene preparation to give 1,3-dichlorobiphenylene as pale yellow needles, m.p. = 72-73°C from ethanol.

Found C, 65.0%; H, 2.7%; Cl, 32.0% $C_{12}H_6Cl_2$

Requires C, 65.2%; H, 2.7%; Cl, 32.1%

4.6 References

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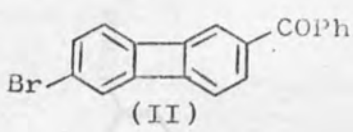
CHAPTER FIVE*

ATTEMPTS TO CHLORINATE SUBSTITUTED BIPHENYLENES

* References for this chapter will be found on page 140.

ATTEMPTS TO CHLORINATE SUBSTITUTED BIPHENYLENES



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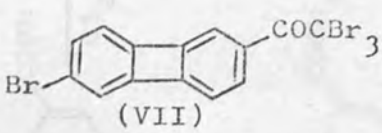

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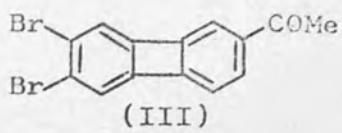


(III)

5.1 Introduction

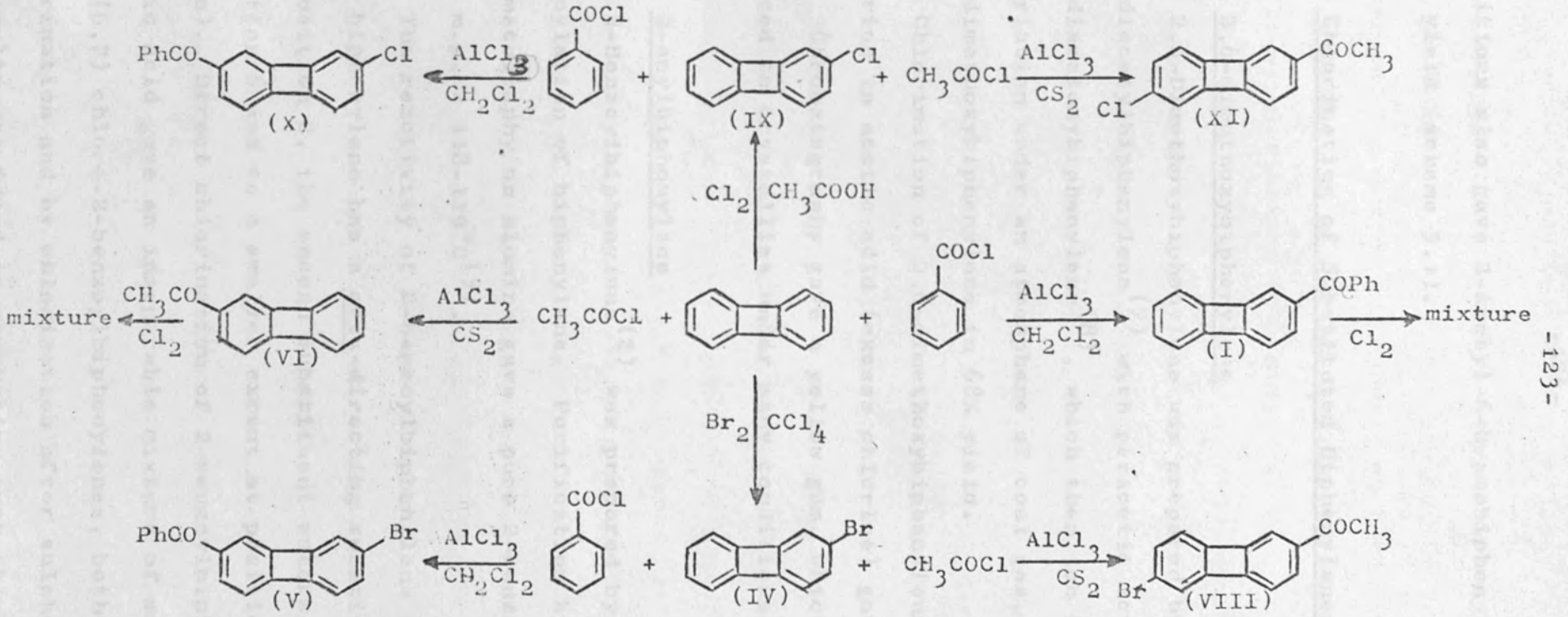
Halogenation of substituted biphenylenes, especially by chlorine, have been very little studied. Direct bromination of 2,6-dimethoxybiphenylene gives the corresponding dibromo-substitution products, even with excess of bromine[1].

Blatchly et al[2] have reported that direct bromination of 2-benzoylbiphenylene (I) gave an inseparable mixture of mono- and dibromo-derivatives, but that when 2-benzoylbiphenylene was first sulphonated and then brominated in acetic acid at 70°C it gave 2-benzoyl-6-bromobiphenylene (II), and, with excess bromine, the 6,7-dibromo-derivative (III).

Benzoylation of 2-bromobiphenylene (IV) by the Friedel-Crafts reaction gave 2-benzoyl-7-bromobiphenylene (V) (scheme 5.1).

Bromination of 2-acetylbiphenylene (VI) again gave an inseparable mixture of mono- and dibromo-derivatives, but after sulphonation provided 6-bromo-2-tribromoacetylbiphenylene[4] (VII).

Recently, Kabli[5] reported that bromination of 2-acetylbiphenylene (VI) by Pearson's method[6] gave also a mixture of 2-acetyl-6,7-dibromobiphenylene and 2-acetyl-6-bromobiphenylene in 9% and 6% yield respectively, but he found that acetylation of 2-bromobiphenylene by Friedel-Crafts



Scheme 5.1

Halogen derivatives of 2-substituted biphenylenes

conditions also gave 2-acetyl-6-bromobiphenylene (VIII) in good yield (scheme 5.1).

5.2 Chlorination of Substituted Biphenylenes

1. 2,6-dimethoxybiphenylene

2,6-Dimethoxybiphenylene was prepared by oxidation of 2,6-diacetylbiphenylene[7] with peracetic acid to give 2,6-diacetoxybiphenylene[8], which then, on hydrolysis and methylation under an atmosphere of coal gas, gave 2,6-dimethoxybiphenylene in 68% yield.

Chlorination of 2,6-dimethoxybiphenylene with molecular chlorine in acetic acid (excess chlorine) gave a black-yellow gum. Chromatography gave a yellow gum, which could not be induced to crystallise under many conditions.

2. 2-acylbiphenylene

2-Benzoylbiphenylene[2] was prepared by Friedel-Crafts benzoylation of biphenylene. Purification by column chromatography on alumina gave a pure 2-benzoylbiphenylene (I), m.p. = 118-119°C[9].

The reactivity of 2-benzoylbiphenylene shows that, as this biphenylene has a meta-directing substituent present at position 2, the second substituent enters mainly at position 6 and to a smaller extent at position 7 (diacetylation). Direct chlorination of 2-benzoylbiphenylene in acetic acid gave an inseparable mixture of mono- (6) and di- (6,7) chloro-2-benzoylbiphenylenes, both by direct chlorination and by chlorination after sulphonation. Great difficulty was found in separating such chlorination

products, and in the desulphonation.

Attempts to separate this mixture by column chromatography on alumina and taking fractions gave first fractions, which were a mixture of mono- and di-chloro-derivatives and last fractions of starting material.

The same result was obtained when 2-acetylbiphenylene[10] was chlorinated in acetic acid at 25°C.

Benzoylation and acetylation of 2-chlorobiphenylene[10] (IX) by Friedel-Crafts reaction in methylene chloride and carbon disulphide respectively gave 2-benzoyl-7-chlorobiphenylene (X) and 2-acetyl-6-chlorobiphenylene (XX). Both were identified by analogy with the benzoylation and acetylation of 2-bromobiphenylene (scheme 5.1).

Blatchly et al[2] have found that bromination of 2-benzoylbiphenylene after sulphonation gave 2-benzoyl-6-bromobiphenylene. The orientation of this compound was proved by converting it via the 6-cyano-derivative, into 2-benzoylbiphenylene-6-carboxylic acid, which was identical with that prepared by oxidation of the furfurylidene derivative of 2-benzoyl-6-acetylbiphenylene. But Kabli[5] has reported that both bromination of 2-acetylbiphenylene and acetylation of 2-bromobiphenylene gave the biphenylene derivative 2-acetyl-6-bromobiphenylene (VIII).

The ultra-violet absorptions of 2-benzoyl-7-chlorobiphenylene (Fig. 5.1) and 2-acetyl-6-chlorobiphenylene are respectively very similar to those of 2-benzoyl-7-bromobiphenylene (Fig. 5.2) and 2-acetyl-6-bromobiphenylene (Table 5.1); and so was the N.M.R. spectra of each pair of compounds (Table 5.2) and (Table 5.3).

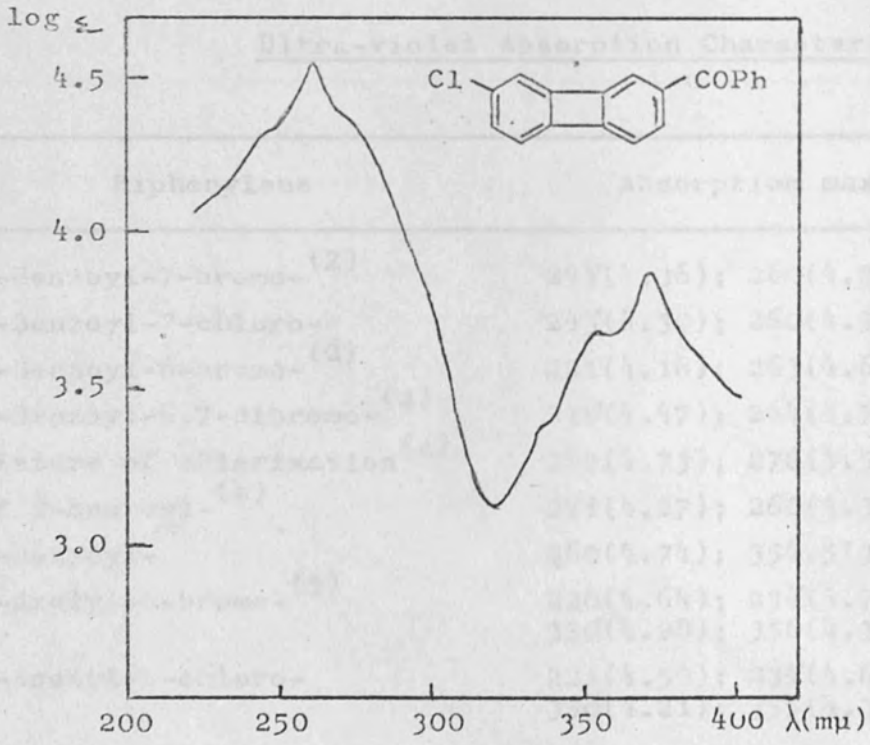


Fig. 5.1

Ultra-violet Absorption of

2-benzoyl-7-chlorobiphenylene in 95% ethanol

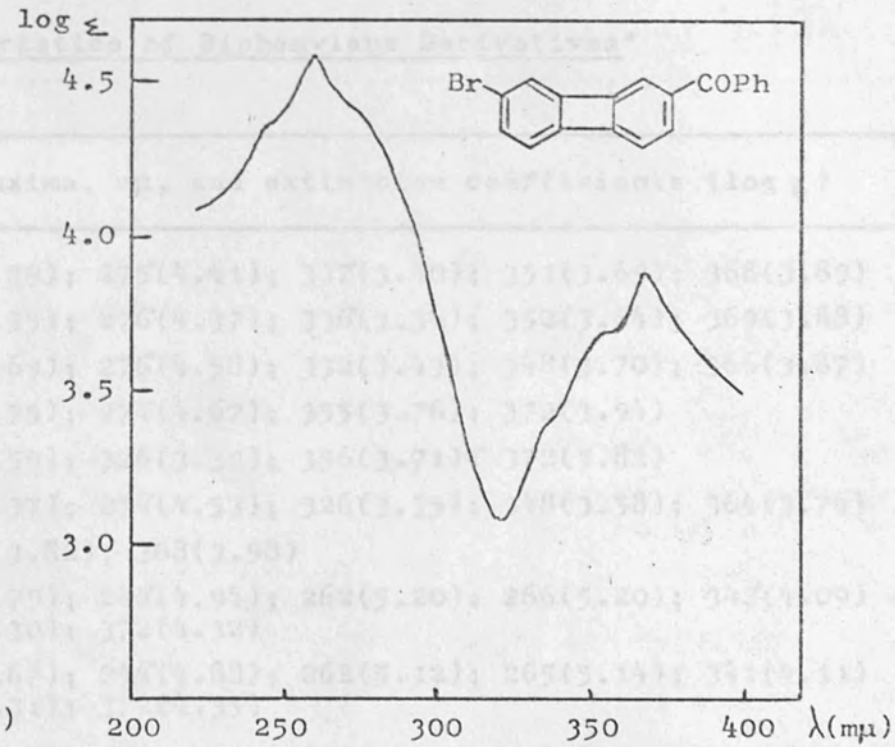


Fig. 5.2

Ultra-violet Absorption of

2-benzoyl-7-bromobiphenylene in 95% ethanol

TABLE 5.1

Ultra-violet Absorption Characteristics of Biphenylene Derivatives*

Biphenylene	Absorption maxima, mμ, and extinction coefficients (log ε)
2-Benzoyl-7-bromo-[2]	244(4.36); 260(4.59); 275(4.41); 337(3.40); 351(3.69); 368(3.89)
2-Benzoyl-7-chloro-	243(4.30); 260(4.55); 276(4.37); 336(3.34); 352(3.64); 369(3.88)
2-Benzoyl-6-bromo-[2]	221(4.16); 263(4.69); 276(4.58); 332(3.43); 348(3.70); 366(3.87)
2-Benzoyl-6,7-dibromo-[2]	249(4.47); 264(4.75); 274(4.67); 355(3.76); 372(3.94)
Mixture of chlorination[a] of 2-benzoyl-[b]	262(4.73); 276(4.59); 326(3.39); 356(3.71); 372(3.82)
2-Benzoyl-[a]	241(4.27); 260(4.37); 274(4.53); 326(3.35); 348(3.58); 364(3.76)
2-Acetyl-6-bromo-[5]	260(4.74); 354.5(3.82); 368(3.98)
2-Acetyl-6-chloro-	220(4.64); 234(4.79); 244(4.94); 262(5.20); 266(5.20); 342(4.09) 350(4.28); 356(4.30); 372(4.32)
	221(4.50); 234(4.67); 244(4.88); 262(5.12); 265(5.14); 341(4.11) 350(4.21); 355(4.31); 372(4.35)

* All the spectra determined in 95% ethanol
• Shoulder or an inflection
(a) chlorination after sulphonation
(b) direct sulphonation

Table 5.2

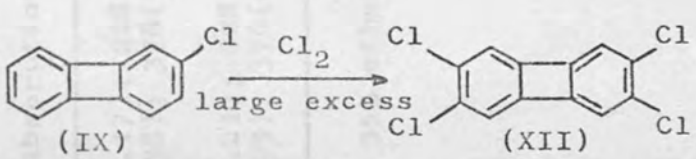
Nuclear Magnetic Resonance of some Substitution·Biphenylenes

Biphenylene	2-Benzoyl-7-bromo-	2-Benzoyl-7-chloro-	2-Acetyl-6-chloro-	2-Acetyl-6-bromo-
(Ph.CO-) τ	2.28-2.72	2.21-2.69	-	-
(CH_3.CO-) τ	-	-	7.62 (s)	7.54 (s)
(1-H, dd.) τ	2.97	2.91	2.79 (t)	2.82 (t)
(3-H, dd.) τ	2.79	2.73	2.50, 2.57 (d)	2.49, 2.56 (d)
(4-H, dd.) τ	3.35	3.40	3.35, 3.50 (d)	3.37, 3.45
(5-H, dd.) τ	3.46	3.44	3.14, 3.20 (d)	3.16, 3.17
(6-H, dd.) τ	3.07	3.03	-	-
(7-H, dd.) τ	-	-	2.90, - 3.03 (d)	2.98, - 3.05 (d)
(8-H, dd.) τ	3.21	3.17	3.22, - 3.27 (d)	3.26, - 3.33 (d)
Coupling Constant (c/sec.)				
$J_{1,3}$	1.20	1.20	1.50	1.50
$J_{1,4}$	0.80	0.90	0.81	0.75
$J_{3,4}$	7.10	7.30	7.40	7.30
$J_{5,6}$	7.40	7.00	-	-
$J_{5,8}$	$\simeq$0.50	$\simeq$0.60	0.80	0.82
$J_{6,8}$	1.50	1.70	-	-
$J_{3,7}$	-	-	1.70	1.50
$J_{7,8}$	-	-	7.60	7.50

3. 2-Halobiphenylenes

Attempts to chlorinate 2-chlorobiphenylene and 2-bromobiphenylene with molecular chlorine in acetic acid, or sulphuryl chloride in chloroform, were unsuccessful. Only starting materials were obtained and green oil fractions, which could not be crystallised under many different conditions.

Although chlorination of 2-chlorobiphenylene (IX) with excess chlorine in acetic acid gave only starting material, but when chlorinated with a large excess of chlorine, also in acetic acid, this time a substituted biphenylene was given as 2,3,6,7-tetrachlorobiphenylene (XII), which was identical with that prepared from pyrolysis of 4,5-dichlorophthalic anhydride[11] and with that prepared by chlorination of biphenylene after sulphonation with sodium chlorate[12], by ultra-violet (Table 5.2) and infra-red spectra.



(IX) (XII)

When 2-chlorobiphenylene was treated with sulphuryl chloride in chloroform it gave a green-black solid, when passed through silica gel, gave starting material and oil fractions, which darkened on standing.

Table 5.2

Ultra-violet Absorption Characteristics of Tetrachlorobiphenylene*

Biphenylene	Absorption maxima, mμ, and extinction coefficient (log ε)
2,3,6,7-tetrachloro-	220°(4.17); 228°(4.10); 246°(4.50); 251(4.85); 261(5.14); 339°(3.62); 359(3.98); 376(4.10).
2,3,6,7-tetrachloro-	220°(4.21); 228°(4.20); 246°(4.56); 251(4.91); 261(5.21); 339°(3.73); 359(3.99); 376(4.21).

* All the spectra determined in 95% ethanol

° Shoulder or inflection.

5.3 Experimental Section

Attempted Chlorination of 2-Benzoylbiphenylene

Preparation of 2-benzoylbiphenylene

2-Benzoylbiphenylene[2][9] was prepared by Friedel-Crafts benzoylation of biphenylene. It was purified by column chromatography on alumina in petroleum ether (b.p. 60-80°C); elution with the same solvent gave unreacted biphenylene. Elution with benzene-petroleum ether (3 : 1) gave 2-benzoylbiphenylene as glistening yellow plates, m.p. = 117-119°C after recrystallisation from ethanol (IR ν_{max} 1640 cm^{-1}).

1. Direct chlorination of 2-benzoylbiphenylene

2-Benzoylbiphenylene (1.28g, 5 mmole) was dissolved in acetic acid (100 ml) and chlorine (0.6g) in the same solvent (10 ml) was added dropwise during 10 minutes.

Then the reaction mixture was left to stand for three hours at room temperature when it was poured into water (500 ml) and the precipitate was collected by filtration. This precipitate (1.43g) was partially separated into its components by passing through an alumina column, applying in benzene and eluting with a mixture of benzene and petroleum ether (b.p. 80-100°C) (2 : 1) and taking 10 ml fractions.

The first fractions were a mixture of mono- and dichloro-derivatives (0.85g) which recrystallised from aqueous ethanol to give yellow crystals, m.p. = 125-192°C.

The last fractions were collected and crystallised from

ethanol to give unreacted 2-benzoylbiphenylene, m.p. = 116-118°C (identified by its U.V. and I.R. spectra).

2. Indirect method (chlorination after sulphonation)

2-Benzoylbiphenylene (2.0g) was dissolved in concentrated sulphuric acid (12 ml). After 24 hours the mixture was poured into water (100 ml). The aqueous solution was stirred at 70°C while chlorine (1.2g) in acetic acid (20 ml) was added dropwise during a 30 minute period, when the reaction mixture was stirred for a further four hours at the same temperature (during the addition of chlorine the yellow colour became pale yellow. By using more chlorine (excess) the pale yellow faded almost completely) and then allowed to cool. The precipitate was collected by extraction with benzene, and the solvent removed under reduced pressure to give a solid (0.53g), m.p. = 120-185°C.

This solid was purified by column chromatography as before, and gave a similar mixture of mono- and dichloro-derivatives (0.23g) and unreacted 2-benzoylbiphenylene (0.16g).

2-Benzoylbiphenylene (1.0g) was sulphonated as before and the sulphonate was poured into water (50 ml). The aqueous solution was stirred at 70°C while chlorine (1.2g) in acetic acid (10 ml) was added gradually during a 45 minute period. Then the reaction mixture was stirred for a further four hours at the same temperature, then allowed to cool. The product was collected by extraction with benzene to give a solid (0.41g) of the same results.

From micro-analysis the mixture appears to contain mostly the monochloro-derivatives.

Found C, 74.10% H, 3.53% Cl, 13.93% mixture of mono- and dichloro-derivatives

Require C, 70.20% H, 3.10% Cl, 21.90% (dichloro-)

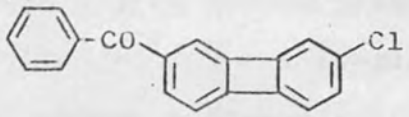
Require C, 78.50% H, 3.80% Cl, 12.20% (monochloro-)

Found C, 73.66% H, 3.86% Cl, 17.13%

Require as above

Benzoylation of 2-chlorobiphenylene

2-Chlorobiphenylene was prepared by different methods (see Chapters 3 and 4).



Powdered aluminium chloride (0.95g) was added gradually during a fifteen minute period to a stirred solution of 2-chlorobiphenylene (0.62g) and benzoyl chloride (0.8 ml) in methylene chloride (30 ml). Stirring was continued for one hour, then the mixture was left over night. Ice cold hydrochloric acid and more methylene chloride (100 ml) were added to the red complex.

Removal of the solvent under reduced pressure gave a yellow solid (1.09g). This was purified by column chromatography on alumina (25 x 2.5 cm) elution with benzene-petroleum ether (b.p. 60-80°C) (2 : 1) to give a pure yellow solid (0.78g). This was recrystallised from ethanol to give glistening bright yellow plates of 2-benzoyl-7-chloro-biphenylene (m.p. = 195-197°C) (I.R. ν_{max} 1640 cm^{-1})

Found C, 78.35% H, 3.80% Cl, 12.19% $C_{19}H_{11}ClO$

Require C, 78.50% H, 3.80% Cl, 12.22%

Attempt to Chlorinate 2-Acetylbiphenylene

Preparation of 2-acetylbiphenylene

2-Acetylbiphenylene[10] was prepared by Friedel-Crafts acetylation of biphenylene.

Powdered aluminium chloride (13g) was added in portions to a stirred solution of biphenylene (4.0g) and acetyl chloride (3 ml) in carbon disulphide (150 ml).

After it had been stirred for four hours the mixture was kept for eight hours, then shaken with ice-cold 3N hydrochloric acid to destroy the red complex.

The product was collected (after filtration to remove the 2,6-diacetylbiphenylene (0.03g)), by removal of the solvent under reduced pressure gave a yellow-brown solid (3.83g). This solid was purified by column chromatography, in n-heptane first to give unreacted biphenylene (0.32g) and then the column was eluted with benzene to give 2-acetylbiphenylene (3.05g) in 61% yield, which recrystallised from aqueous ethanol, giving the pure compound as glistening yellow plates, m.p. = 133-135°C (lit[4][10] 134-135, 132-134°).

1. Direct chlorination of 2-acetylbiphenylene

2-Acetylbiphenylene (2.0g) was dissolved in glacial acetic acid (100 ml). Chlorine (1.0g) in acetic acid (10 ml) was added gradually during a ten minute period. The reaction mixture was left to stand over night. It was then poured into water (500 ml) and the precipitate was collected by filtration. This precipitate (2.39g) was subjected to chromatography on an alumina column applying in benzene and eluting with a mixture of benzene and petroleum ether

(b.p. 60-80°C) (4 : 1) and taking 10 ml fractions.

The first fractions were a mixture of mono- and dichloro-derivatives (1.2g) which recrystallised from ethanol to obtain yellow crystals, m.p. = 230°C (decomposed).

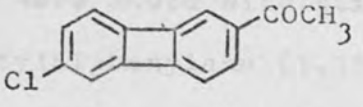
The last fractions were collected and crystallised from aqueous ethanol to give unreacted 2-acetylbiphenylene (0.11g), m.p. = 132-134°C (identified by its U.V. and I.R. spectra).

2. Chlorination of 2-acetylbiphenylene after sulphonation (Indirect)

2-Acetylbiphenylene (1.0g) was dissolved in concentrated sulphuric acid (40 ml) and the solution was kept at room temperature for 24 hours. Then it was poured into water (100 ml) and chlorine (1.2g) in glacial acetic acid (10 ml) was added dropwise during twenty minutes. The reaction mixture was stirred at 70°C. After being stirred for a further three hours, cooling gave a few milligrams of precipitate.

Extraction of the cold solution with benzene and evaporating the solvent under reduced pressure gave a solid (0.05g) which appeared to be a mixture.

Acetylation of 2-chlorobiphenylene



Powdered aluminium chloride (1.42g) was added in portions during a twenty minute period to a solution of 2-chlorobiphenylene (0.94g) and acetyl chloride (1 ml) in

carbon disulphide (20 ml). The reaction mixture was stirred for two hours, then cooled to 0°C, then ice-cold dilute hydrochloric acid (40 ml) was added with shaking until all the red complex was destroyed. Evaporating the solvent under reduced pressure gave a dark brown-yellow solid which was purified by column chromatography on alumina with benzene to give pure 2-acetyl-6-chlorobiphenylene, m.p. = 127-129°C as yellow plates after recrystallisation from ethanol (ν_{max} C=O 1640 cm^{-1})

Found	C, 73.73%	H, 3.50%	Cl, 15.80%	$C_{14}H_9ClO$
Require	C, 73.50%	H, 3.90%	Cl, 15.50%	

Attempted Chlorination of 2,6-Dimethoxybiphenylene

1. Preparation of 2,6-diacetylbiphenylene

2,6-Diacetylbiphenylene[10] was prepared by diacetylation of biphenylene by the Friedel-Crafts reaction. It was purified by column chromatography on silica gel; eluting with benzene gave the pure compound. This was recrystallised from benzene-chloroform (1 : 1) as yellow needles, m.p. and mixed m.p.[4][10] = 252-254°C (ν_{max} C=O 1676 cm^{-1})

2. Preparation of 2,6-diacetoxybiphenylene[8]

Peracetic acid (36-40%; 70 ml) and then concentrated sulphuric acid (0.5 ml) were added with stirring to a fine suspension of 2,6-diacetylbiphenylene (1.35g) in acetic acid (70 ml) (the solid diketone was slightly soluble in acetic acid) and the mixture was stirred for a further six hours at 35°C.

The mixture was then cooled to 0°C giving 2,6-diacetoxy-

biphenylene (0.6g) as faintly yellow plates, m.p. = 200-202°C (decomposed) from acetone.

3. Preparation of 2,6-dimethoxybiphenylene

Potassium hydroxide (10g) in water (10 ml) was added with stirring during fifteen minutes to a solution of 2,6-diacetoxybiphenylene (0.5g) in methanol (10 ml) and dimethyl sulphate (10 ml) under an atmosphere of nitrogen gas. At first, after each addition of alkali, the solution showed a sequence of colour, from red to yellow.

After all the alkali had been added the mixture was boiled for ten minutes, then cooled and diluted with water (100 ml) to give a solid which was purified by chromatography on alumina column using benzene-petroleum ether (b.p. 60-80°C) (1 : 1).

Elution gave a solid which recrystallised from methanol to give pure 2,6-dimethoxybiphenylene (0.32g) as lemon-yellow plates, m.p. = 130-132°C.

Chlorination of 2,6-dimethoxybiphenylene

2,6-Dimethoxybiphenylene (0.106g) was dissolved in glacial acetic acid (10 ml), chlorine (0.08g) in acetic acid (5 ml) was added gradually, and after half an hour the reaction mixture was poured into water (100 ml), extracted with ether and the organic phase was dried over magnesium sulphate. Evaporating the solvent under reduced pressure gave a black to dark green gum which was never adequately purified by column chromatography on either alumina or silica gel.

Chlorination of 2-Chlorobiphenylene

2-Chlorobiphenylene was prepared by chlorination with molecular chlorine or with sulphuryl chloride (Chapter 3), and was purified by recrystallisation from aqueous methanol to give the pure compound, m.p. = 66-67°C

2-Chlorobiphenylene (0.47g) was dissolved in chloroform (7 ml). Then sulphuryl chloride (for purification of sulphuryl chloride see Chapter 2) (0.3 ml) was added and the reaction mixture was left standing for a week or boiled under reflux for three hours. It was then poured into water to destroy the excess of sulphuryl chloride, and the residue was extracted with ether and the extract dried over magnesium sulphate.

Removing the solvent under reduced pressure left a green-black solid (0.52g). This was purified by column chromatography on silica gel; elution with n-heptane gave first the starting material (0.24g), m.p. = 66-67°C, then an oil fraction which darkened on standing, but did not give crystalline material.

2-Chlorobiphenylene (0.93g) was dissolved in glacial acetic acid (10 ml). Chlorine (0.5g) in the same solvent (5 ml) was added gradually during a five minute period. The reaction mixture was kept over night. The mixture was then poured into water (200 ml), extracted with ether, and the extract dried over magnesium sulphate.

Removing the solvent under reduced pressure left a pale black solid (1.12g). This was purified by column chromatography on silica gel; elution with petroleum ether (b.p. 40-60°C) gave first starting material (0.75g) then oil fractions which again darkened on standing, but

did not give a crystalline material.

The same result was obtained in chlorination of 2-bromobiphenylene[10] with molecular chlorine and sulphuryl chloride at room temperature, in acetic acid and chloroform respectively.

Chlorination of 2-Chlorobiphenylene with large excess of Chlorine

2-Chlorobiphenylene (0.47g, 0.0025 mole) in glacial acetic acid (10 ml). Chlorine (2.0g, 0.028 mole) in acetic acid (20 ml) was added dropwise during a ten minute period.

The reaction mixture was kept standing for two hours and gave a deposit of pale yellow needles. These were collected by filtration, washed with water and dried. These, on recrystallisation from benzene, gave 2,3,6,7-tetrachlorobiphenylene as pale yellow needles, m.p. = 300-301°C (0.31g, 62%). Dilution of the mother liquor from the reaction mixture gave another few milligrams of tetrachlorobiphenylene.

Found C, 49.49%; H, 1.48% $C_{12}H_4Cl_4$

Require H, 49.66%; H, 1.38%.

(The I.R. spectrum showed a strong band at 876 cm^{-1}, characteristic of a single aromatic C-H deformation).

5.4 References

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APPENDIX

METHODS OF CALCULATION

ULTRA-VIOLET SPECTRAL ANALYSIS OF MIXTURES OF DERIVATIVES OF BIPHENYLENE

The U.V. spectra of biphenylenes show absorptions at 340-360 mμ (27800-29400 cm^{-1}). In a reaction mixture in which the biphenylene A and its chlorination product, B, are present, the U.V. absorption in this region is only due to A and B, and not to the presence of any addition or decomposition products. The optical density of a solution of such a mixture is therefore composed of two terms:

$$\log_{10} I_o/I = \Sigma_A.C_A.d + \Sigma_B.C_B.d$$

Rearrangement of this gives

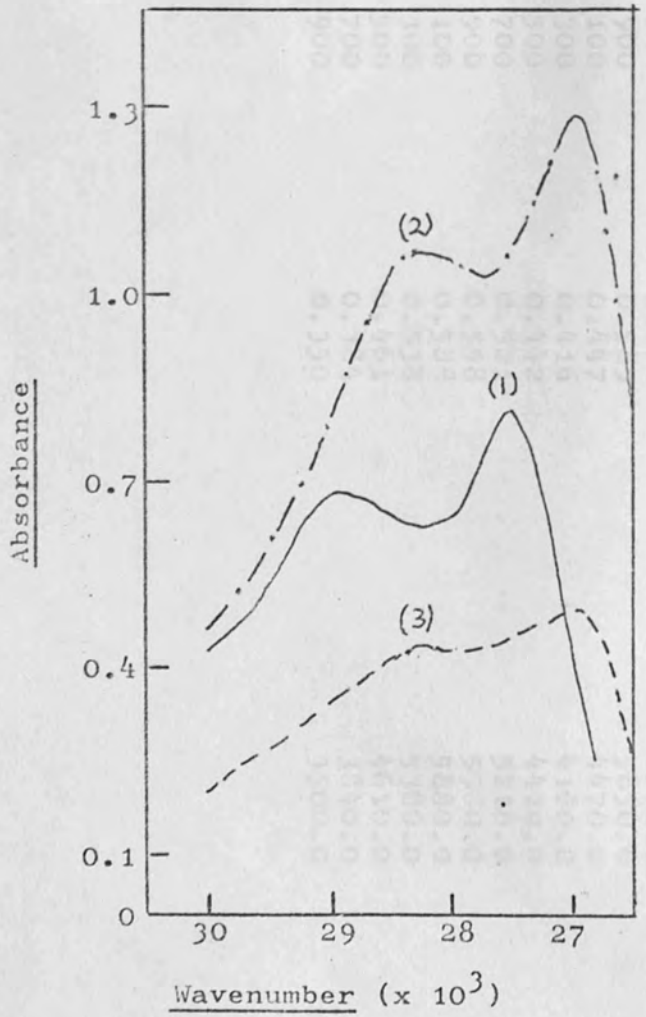
$$(\log_{10} I_o/I)/\Sigma_A.d = C_A + (\Sigma_B/\Sigma_A).C_B$$

The extinction coefficients, $_A$ and $_B$, can be measured at individual wavelengths, using solutions of pure A and pure B. The optical density of the reaction mixture can be similarly measured at these wavelengths. The equ tion is now a graph in the form, y = c + mx. Individual values of $(\log_{10} I_o/I)/\Sigma_A.d)$ are plotted against (Σ_B/Σ_A) at each wavelength, to give a graph of slope C_B and intercept C_A.

The assumption of two biphenylene components only is shown by the fit of the straight line; when more than one biphenylene is formed, this graphical method cannot be applied.

For the chlorination of 2-methoxybiphenylene in acetic acid at 25°C, (Fig. 2, Graph 2), the slope is (6.73-4.89) x $10^{-5}/0.4 = 4.6 \times 10^{-5}$ M = (2-MeO-3-Cl.$C_{12}H_6$). The intercept of this graph gives (2-MeO.$C_{12}H_7$) = 1.67×10^{-5} M. As the initial concentration was 10^{-3} M, this corresponds to 4.6% yield.

Fig. 2


Absorbance
1.3
1.0
0.7
0.4
0.1
0
(1)
(2)
(3)
30
29
28
27
Wavenumber (x 10^3)

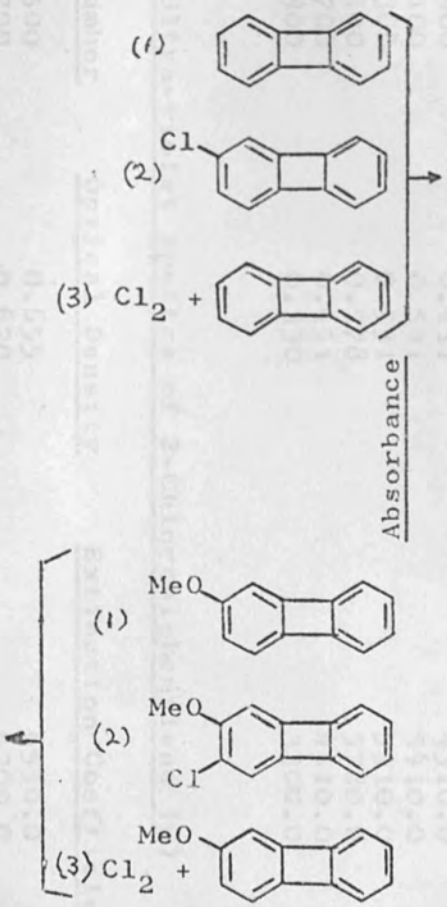
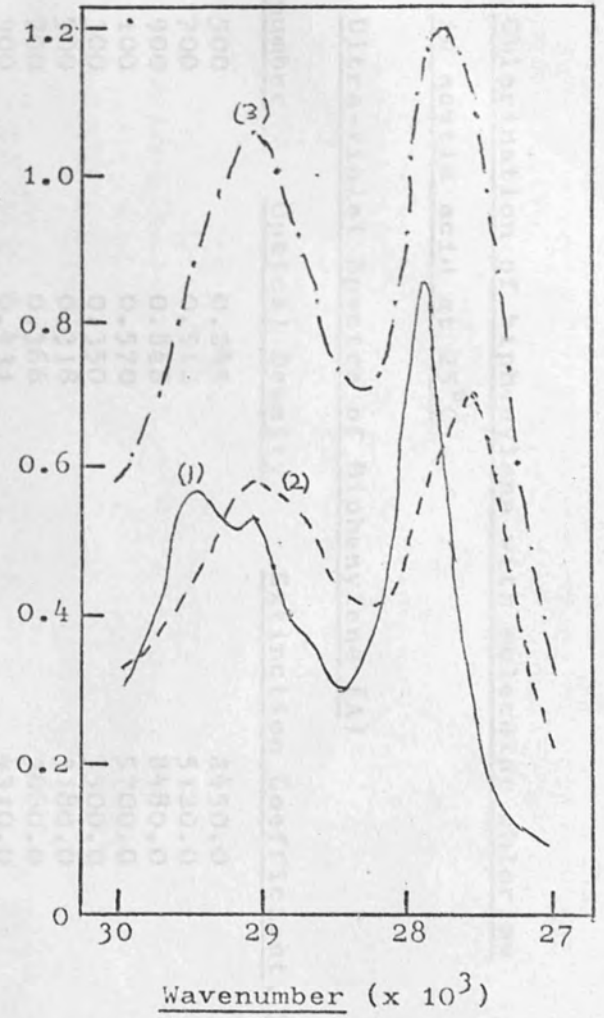

(1)
Cl
(2)
(3) Cl_2 +
MeO
(1)
MeO
(2)
Cl
MeO
(3) Cl_2 +

Fig. 1


Absorbance
1.2
1.0
0.8
0.6
0.4
0.2
0
(1)
(2)
(3)
30
29
28
27
Wavenumber (x 10^3)

1. Chlorination of biphenylene with molecular chlorine in acetic acid at 25°C

I Ultra-violet Spectra of Biphenylene (A)

Wavenumber	Optical Density	Extinction Coefficient, Σ_A
27 500	0.245	2450.0
700	0.512	5120.0
900	0.848	8480.0
28 100	0.570	5700.0
300	0.350	3500.0
500	0.318	3180.0
700	0.366	3660.0
900	0.431	4310.0
29 100	0.541	5410.0
300	0.531	5310.0
500	0.578	5780.0
700	0.451	4510.0
900	0.330	3300.0

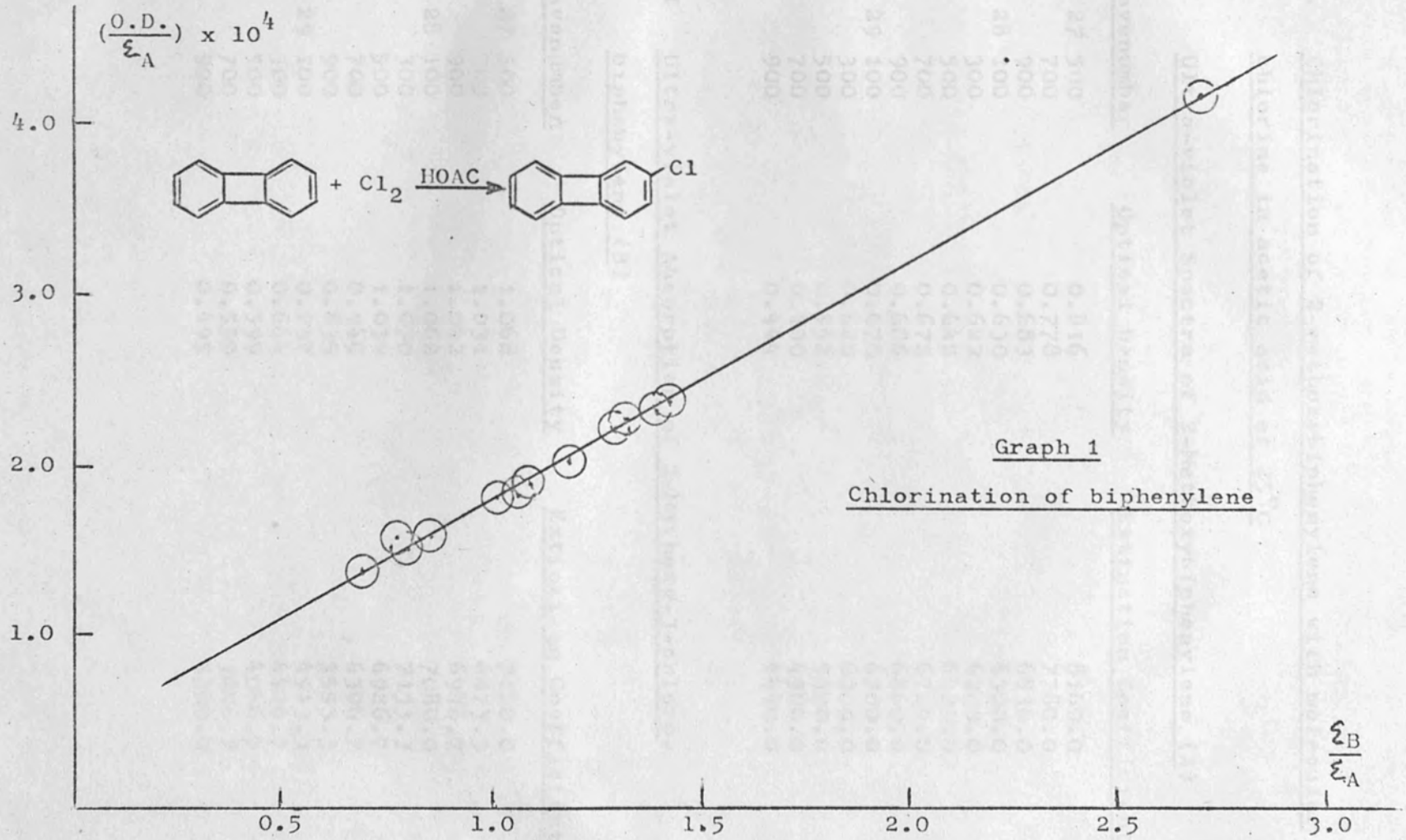
II Ultra-violet Spectra of 2-Chlorobiphenylene (B)

Wavenumber	Optical Density	Extinction Coefficient, Σ_B
27 500	0.655	6550.0
700	0.670	6700.0
900	0.585	5850.0
28 100	0.447	4470.0
300	0.416	4160.0
500	0.442	4420.0
700	0.521	5210.0
900	0.558	5580.0
29 100	0.588	5880.0
300	0.538	5380.0
500	0.461	4610.0
700	0.384	3840.0
900	0.350	3500.0

1. (continued)

III Ultra-violet Spectra of Reaction Mixture

Wavenumber	Optical Density	$\frac{O.D.}{\Sigma_A} \times 10^{-5}$	$\frac{\Sigma_B}{\Sigma_A}$
27 500	1.030	4.2041	2.6735
700	1.182	2.3086	1.3086
900	1.184	1.3962	0.6899
28 100	0.861	1.5105	0.7842
300	0.718	2.0514	1.1886
500	0.740	2.3270	1.3899
700	0.887	2.4235	1.4235
900	0.970	2.2506	1.2947
29 100	1.064	1.9667	1.0869
300	0.990	1.8644	1.0132
500	0.892	1.5433	0.7976
700	0.724	1.6053	0.8514
900	0.622	1.8848	1.0606



Graph 1

Chlorination of biphenylene

2. Chlorination of 2-methoxybiphenylene with molecular chlorine in acetic acid at 25°C

I Ultra-violet Spectra of 2-Methoxybiphenylene (A)

Wavenumber	Optical Density	Extinction Coefficient, Σ_A
27 500	0.816	8160.0
700	0.778	7780.0
900	0.683	6830.0
28 100	0.630	6300.0
300	0.622	6220.0
500	0.642	6420.0
700	0.672	6720.0
900	0.686	6860.0
29 100	0.670	6700.0
300	0.620	6200.0
500	0.552	5520.0
700	0.490	4900.0
900	0.444	4440.0

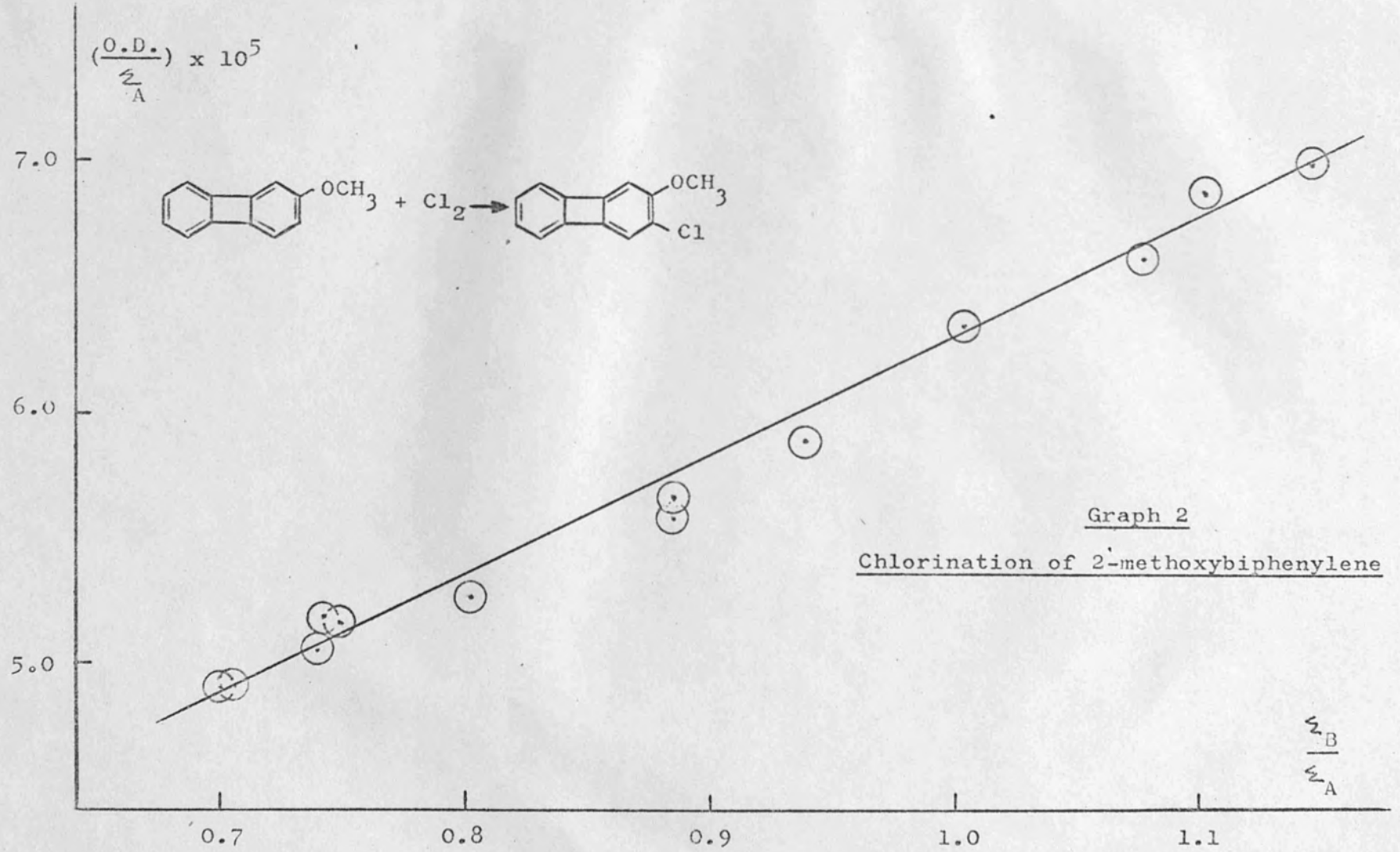
II Ultra-violet Absorption of 2-Methoxy-3-chloro-biphenylene (B)

Wavenumber	Optical Density	Extinction Coefficient, Σ_B
27 500	1.068	7120.0
700	1.031	6873.3
900	1.042	6946.7
28 100	1.062	7080.0
300	1.070	7133.3
500	1.039	6926.7
700	0.946	6306.7
900	0.835	5553.3
29 100	0.737	4913.3
300	0.664	4426.7
500	0.599	4066.7
700	0.550	3666.7
900	0.495	3300.0

2. (continued)

III Ultra-violet Spectra of Reaction Mixture

Wavenumber	Optical Density	$\frac{O.D.}{\Sigma_A} \times 10^{-5}$	$\frac{\Sigma_B}{\Sigma_A}$
27 500	0.455	5.5760	0.8836
700	0.439	5.6426	0.8835
900	0.433	6.3396	1.0171
28 100	0.433	6.8730	1.1238
300	0.430	6.9614	1.1468
500	0.425	6.6200	1.0789
700	0.392	5.8779	0.9385
900	0.361	5.2547	0.8095
29 100	0.330	4.9180	0.7332
300	0.305	4.9194	0.7400
500	0.279	5.0543	0.7367
700	0.253	5.1633	0.7483
900	0.230	5.1800	0.7432



Graph 2

Chlorination of 2-methoxybiphenylene